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Comparison of Weekly and Daily Wet Deposition Sampling Results Supplemental Report, December 1986

Environmental Monitoring and Services, Inc.
Camarillo, CA

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

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This report presents the results of a joint effort by the U.S. EPA and the Electric Power Research Institute.

16. ABSTRACT
A collocated sampling study was conducted at three Utility Acid Precipitation Study Program sites (Uvalda, GA; [illegible]caster, KS; Underhill, VT). Each site was equipped with four identical precipi[illegible] samplers, two collecting daily samples and the other two collecting weekly [illegible]s. Except for the sampling schedule, all other procedures (e.g., sample tra[illegible] storage, analysis) were the same. This study determined the effect of samplin[illegible]uency on: collection efficiency, the precision and chemical composition of the sample, the assessment of deposition amount, and the time required to detect trends in concentration and deposition. These results are reported in this document.

The report will be published by the Utility Acid Precipitation Study Program.

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Comparison of Weekly and Daily Wet Deposition Sampling Results

UAPSP 113
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UTILITY ACID PRECIPITATION STUDY PROGRAM

Comparison of Weekly and Daily Wet Deposition Sampling Results

UAPSP 113
Contract U101-1

Supplemental Report, December 1986

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Combustion Engineering Environmental Monitoring and Services, Inc.
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UAPSP PERSPECTIVE

The Utility Acid Precipitation Study Program (UAPSP) was established in 1981 to ensure that daily precipitation chemistry data of quantified accuracy and precision would be available. The use of such data would include the evaluation of temporal and geographic variabilities and trends in relation to emissions. Other precipitation sampling networks in the United States generally collect either daily or weekly samples. The choice of sampling frequency has always been a difficult one often determined by available resources. It has been assumed that weekly sampling is sufficient for determining long-term trends and ecological exposures, and that daily sampling is only necessary if one wished to explore source-to-receptor relationships. Because combining data sets would enhance their usefulness, it is important to determine the comparability of these two sampling frequencies.

Although a number of recent studies have compared weekly and daily samples, interpreting the results is complicated by the use of different equipment, operators, and laboratories analyzing the samples. Therefore, beginning in October 1983, the Utility Acid Precipitation Study Program (UAPSP) and the U.S. Environmental Protection Agency jointly sponsored a collocated field study to provide a direct assessment of the effect of sampling frequency. Specifically, the objectives of this study were to determine the efficiency of the collectors, the precision and composition of daily and weekly samples, and to compare the concentration and deposition obtained from daily and weekly samples.

This study was designed to overcome previous limitations and focused on the differences in sampling frequency only. It is unique in several ways. First, three UAPSP sites (Georgia, Kansas, and Vermont) were selected to represent different geographical, climatic, and chemical (i.e., rain chemistry) regions. Second, the study was conducted for one full year. Third, four identical precipitation samplers (two daily and two weekly) were operated at each site to determine the precision of both sampling frequencies as well as the comparison between daily and weekly measured chemistry. Fourth, collocated rain gauges were

operated at two sites (Kansas and Vermont) to determine the precision of precipitation depth and deposition. Fifth, all chemical analyses were performed in the same laboratory. Finally the concentration data were screened for extreme values and missing data prior to their analysis. However, a method accounting for missing daily deposition values remains to be successfully established.

According to the findings, the differences in concentrations reported for weekly and daily sampling are not large. Nevertheless, detectable biases exist which deserve attention when weekly and daily data are combined. To what extent such biases may be exacerbated when other procedural differences among networks are also considered remains to be studied. The ability to detect annual trends in precipitation composition is enhanced by daily sampling. Moreover, daily data appear to be more reliable for estimating differences among seasons. Taken individually, daily and weekly sampling will provide consistent spatial distributions but, when combined, may alter or add noise to these distributions. Therefore, a network that changes its sampling frequency would create a bias that could interfere with the detection of trends.

This first study of how sampling frequency alone influences precipitation chemistry data, should be useful to data analysts. In addition, network managers will now be in a better position to assess the effectiveness of their sampling protocol in meeting network objectives in comparison with costs.

John J. Jansen
Southern Company Services, Inc.
Chairman, UAPSP Technical Review Committee

LIST OF UAPSP AND EPRI PUBLISHED REPORTS ON PRECIPITATION CHEMISTRY

This report is one of a series of reports on the Utility Acid Precipitation Study Program (UAPSP). To give the reader an easy reference to other reports on UAPSP and related EPRI reports, the following list is presented. UAPSP reports can be obtained through the UAPSP Report Center (see copyright page for further ordering information), unless indicated otherwise. Copies of the EPRI reports can be obtained through the EPRI Research Reports Center (RRC), Box 50490, Palo Alto, CA 94303, (415) 965-4081.

Report Number	Project Number	Title	Publication Date
UAPSP Reports			
100	U101-00	Proceedings: Advisory Workshop on Methods for Comparing Precipitation Chemistry Data	February 1983
101	U101-90	1982 Annual Summary Report	February 1983
102	U101-01	UAPSP Laboratory Standard Operating Procedures	March 1983 (1)
103	U101-01	UAPSP Precipitation Data Displays for January 1, 1979-June 30, 1982 Volumes 1 & 2	August 1983
104	U101-01	The Utility Acid Precipitation Study Program: Field Operator Instruction Manual	January 1983 (1)
105	U101-01	The Utility Acid Precipitation Study Program: Network Description and Measurements for 1981 and 1982, Volumes 1 & 2	November 1986
106	U101-01	Plan for Controlling the Quality of Measurements and Data Base During the Utility Acid Precipitation Study Program (UAPSP)	September 1982 (2)
107	U101-02	1982 Quality Assurance Summary Report for the Utility Acid Precipitation Study Program	March 1983 (1)
108	U101-01	Description and Format of Data Base for EPRI (UAPSP) Acid Precipitation Measurements	April 1983 (2)

109	U101-90	UAPSP Second Summary Report	September 1984
111	U101-04	The Influence of Meteorological Factors on Precipitation Chemistry	November 1986
112	U101-03	Statistical Analysis of Precipitation Chemistry Measurements over the Eastern United States	June 1986
113	U101-01	Comparison of Weekly and Daily Wet Deposition Sampling Results	November 1986

EPRI Related Reports

EA-1914 (vol 2)	1630-01	Precipitation Scavenging Chemistry for Sulfate and Nitrate from the SURE and Related Data	February 1983
EA-1751	1630-02	Precipitation Chemistry Measurements in the SURE Region	(in press)
EA-4663	1630-52	Proceedings: Methods for Acidic Deposition Measurement	August 1986

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(1) Available on request from EPRI Project Manager
(2) Available on request as a working document from the EPRI Project Manager. Subject to revisions.

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SUMMARY

The objectives of this study were to evaluate the changes in chemical composition that may occur when precipitation is stored up to seven days in collectors, and to assess the significance of the variability of those changes from site to site and among seasons. In a one-year field program, two pairs of identical wet deposition samplers were deployed at three sites (in Georgia, Kansas and Vermont), and for each predesignated pair either daily samples or weekly samples were collected. The Kansas and Vermont sites also had a pair of collocated weighing-bucket rain gauges. The results of this study provide a direct assessment of differences in sampling schedule since common procedures were used at all three field sites and all samples were analyzed at the same laboratory.

The data collected were screened and validated prior to data analysis. Samples were considered invalid if there was obvious contamination. Concentrations were also missing for low-volume events and when there was a sampler malfunction. In order to ensure that the results are not overly influenced by extreme values, an outlier detection and rejection scheme, based on three standard deviations around the mean of the collocated sampler differences at each site, was utilized. Whenever possible, nonparametric statistical techniques, which are less sensitive to outliers than parametric techniques, were used to assess statistical significance.

The data obtained were used to determine differences between daily and weekly sampling for (a) collection efficiency (by reference to the same rain gauge) for each site and by precipitation type, (b) precision of daily and weekly monitoring, (c) concentration bias, expressed as the relative difference between derived weekly and measured weekly concentrations, overall and by season, and (d) deposition bias, defined as the difference between the deposition calculated from the daily measurements and that from the weekly measurements. The major results of this investigation are given below.

- The collection efficiencies were highest for rain and about equal for snow and mixed precipitation with a value of about 1.1 for rain and 0.75 for mixed and snow. Generally small differences were observed between weekly and daily sampling and among sites for the same precipitation type.

- The precision of ionic concentration determinations is either comparable or better for daily than for weekly samples. Overall measurement precision for both sampling protocols (with the exception of potassium) is less than 20 percent of ionic concentrations.

- The measured weekly concentrations were, in most cases, approximately 10 percent higher than the weekly concentrations derived from daily samples.

- The differences between weekly and composited daily concentrations varied by constituents, but they were in general less than 10 percent of the mean concentration. Also, the individual ion concentration biases are of similar magnitudes and direction among the sites with the exception of acidity and sodium.

- There is seasonal variation in the concentration bias between daily composited and weekly samples. Concentrations of all ions except ammonium were significantly higher in the fall for the weekly measurements. Concentrations of calcium and nitrate were significantly higher in weekly measurements in the spring. No statistically significant biases were observed for the summer quarter.

- Differences in paired rain gauge depths at the two sites with collocated rain gauges were greatest for snow samples. Overall, the paired rain gauges at the Vermont site measured significantly different precipitation amounts; the differences were greatest in the winter quarter. The significant differences in rain gauge depth resulted in significant differences in daily deposition for all ions except potassium at the Vermont site.

- Precision of daily depositions (calculated from the two daily collectors and the two rain gauges) was better at the Kansas site; for most ions the precision was 5 to 15 percent. At the Vermont site, where the rain gauge differences were larger, the precision of ion depositions were 10 to 30 percent (as measured by relative absolute collocated difference).

- Deposition bias, the difference between deposition calculated from daily and weekly measurements, remains to be examined. A method must first be established to adjust daily data for missing values.

- Calculated deposition amounts vary by season at each site. Peak sulfate deposition occurred in the spring at the Kansas and Georgia sites, and in the summer at the Vermont site. Peak acidity deposition values occurred in the summer at the Vermont and Georgia sites, and in the spring at the Kansas site.

In conclusion, the comparison of measurement errors demonstrated that ionic concentrations of daily collected samples can be determined with better precision than those of samples collected weekly for most constituents. Therefore, daily sample collection provides narrower confidence intervals for concentration means and allows earlier detection of significant trends in precipitation composition. In addition, measured weekly concentrations were generally higher than weekly concentrations derived from daily samples. However, the seasonal variability in the results obtained from daily versus weekly sampling was not consistent either in magnitude or direction. This indicates that daily and weekly sample collection provides consistent spatial distribution results (at least for the three sites studied), while temporal distributions obtained from weekly samples might be incompatible with those obtained from daily samples. Therefore, for a network that changes from daily to weekly sampling, the bias in the results will interfere with trend analysis. Finally, it must be noted that in this study all field and laboratory procedures were identical for daily and weekly sample collection. Different results might be obtained in comparing data from two different networks where differences in both sampling schedules and field and laboratory procedures exist.

Section 1

INTRODUCTION

Precipitation sampling networks in the United States generally collect either daily (UAPSP, MAP3S) or weekly (NADP/NTN) samples. Under a weekly schedule, samples can remain in the collector under ambient conditions for up to seven days, possibly resulting in more chemical changes than might occur if the samples remain in collectors for at most 24 hours. It is important to know the occurrence and magnitude of such changes when comparing chemical composition and trends calculated from weekly and daily deposition networks.

To determine the importance of any such chemical changes, a collocated sampling study was performed by Environmental Monitoring and Services, Inc. (EMSI) at three sites of the Utility Acid Precipitation Study Program (UAPSP) network from October 1983 to October 1984. The sites--at Uvalda, Georgia; Lancaster, Kansas; and Underhill, Vermont--were selected to represent the southeastern, central (west of the Mississippi River), and northeastern regions of the United States.

The objectives of the study were to determine the efficiency of the collectors, to quantify the precision and composition of daily and weekly samples, and to compare the concentrations and depositions obtained from weekly and daily samples. For this study a daily sample is the total precipitation in a 24-hour period, starting at about 0900 LST. A weekly sample is the total precipitation collected in the period from 0900 of the sample pick-up day, generally Monday, to the same time and day of the following week.

Four studies comparing weekly versus daily (or event) samples have recently been performed using the same type of samplers as in the present study: at one MAP3S site at Pennsylvania State University (1), at one NADP site at North Carolina State University (2), at Argonne National Laboratory (3), and at one Florida site (4). The Penn State study utilized two samplers, one collecting daily samples and the other, weekly samples. All analyses were performed by Battelle Pacific Northwest Laboratory. The weekly samples had lower concentrations and deposition values for all the ions analyzed, acidity (H^+), sulfate ($SO_4^=$), nitrate (NO_3^-),

ammonium (NH_4^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}). The study at North Carolina State involved four daily collectors and six weekly collectors of wet precipitation. The data from this study were used primarily to compare collection efficiencies as a function of the collector's distance from the rain gauge. However, the data indicate that gross chemical changes, as evidenced by pH and specific conductance, did not occur over collection periods of one week, although the possibility of chemical changes in other analytes cannot be ruled out by the available data. In the Argonne study two samplers activated by a single sensor were operated for approximately two years. This approach assured simultaneous opening and closing of both collectors. The ions measured were the same as in the Penn State study; the weekly samples were analyzed by the Illinois State Water Survey, whereas the event samples were analyzed by Argonne. This study found that weekly samples had significantly less NH_4^+ and H^+ in all seasons and more $SO_4^=$ in every season but summer. Weekly samples had significantly more Ca^{2+} and Mg^{2+} during seasons with little precipitation. No significant differences between weekly and event NO_3^- were evident. In the Florida study three samples collected wet precipitation on a daily, weekly, and biweekly schedule for one year. All analyses were performed at the University of Central Florida within ten days of collection. No statistically significant differences in precipitation composition with sampling interval were found.

Interpreting the results of these and other (older) studies is complicated by the fact that most studies used different equipment and operators, and different laboratories doing the measurements. The present study was designed to control these complicating factors and focus on the differences in sampling period only. This study is unique in several ways. Three regular UAPSP monitoring sites were equipped with four identical precipitation samplers, two collecting daily samples, and two, weekly samples. This allows precision data to be calculated for both sampling schedules as well as a comparison of the chemical composition of the daily and weekly samples. All analyses were performed in the same laboratory. Except for the sampling schedule, all procedures were identical. Two sites had collocated rain gauges so that the precision of precipitation depth and deposition could also be determined.

A discussion of the sampling sites and sampling period is given in Section 2. The site equipment and operations and the laboratory operations are described in Section 3. Data management, including data processing, outlier screening, and statistical tests, is covered in Section 4, and the results are presented and discussed in Section 5. The conclusions of this study are presented in Section 6.

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Section 2

SAMPLING SITES AND PERIOD

In this section the monitoring sites are described and their conformance to the UAPSP site selection criteria is discussed. To demonstrate site conformance to the criteria, a source emission inventory is included.

SITE SELECTION CRITERIA

Criteria used for site selection for precipitation monitoring are outlined in the U.S. EPA Quality Assurance Manual for Precipitation Measurement Systems (1). Primary criteria adopted for the UAPSP network were the following:

- No large point emission or urban sources located within 20 km;
- Grassy areas at the sites to minimize splash;
- No obstructions, including overhead wires, that might cast rain or wind shadows on the site and serve as sources of contamination (nonrepresentative data caused by obstructions can be avoided by ensuring that the distance between any tall object and the collector or rain gauge is at least twice the difference between the height of the object and the collector);
- Fairly flat land to assure level positioning of equipment and to minimize snow drift problems;
- Proximity to the operators' homes or jobs and ready accessibility to facilitate the required daily visits;
- No storage of agricultural products, fuels, or other foreign materials within 100 m.

Secondary considerations were

- Location at least 20 m from all mobile or small local sources, such as roads, crop fields, or grazing animals, or at least upwind of these sources; and

- The presence of trees to act as a windbreak.

These siting criteria are similar to those of the MAP3S network (2), the National Atmospheric Deposition Program (NADP) (3), and the EPRI-SURE study (4). One exception is that NADP requires a 5 m separation between the collector (1.5 m in height) and rain gauge; this criterion is more severe than for other obstructions, for which NADP accepts a separation distance equal to the height of the object. The 1.5 m spacing between collocated samplers and between samplers and rain gauges was used in this study. The conformance of the UAPSP sites to the siting criteria is discussed below.

For this study three sites from the UAPSP network that typified different regions and climates of the eastern United States were selected. These sites were Uvalda, GA (Site 14), in the Southeast; Lancaster, KS (Site 18), west of the Mississippi River; and Underhill, VT (Site 20), in the Northeast. The coordinates and elevations of the three sites are listed in Table 2-1.

Table 2-1

COORDINATES AND ELEVATION OF COLLOCATION STUDY SITES

Site No.	Location	Latitude	Longitude	Elevation (m)
14	Uvalda, GA	32° 03' 18"	82° 28' 25"	64
18	Lancaster, KS	39° 34' 10"	95° 18' 17"	346
20	Underhill, VT	44° 31' 42"	72° 52' 08"	442

SITE DESCRIPTIONS

In order to determine whether the study sites met the source distance criterion, important point sources within 50 km of each site were identified using the U.S. EPA's 1977-78 National Emissions Data Systems (NEDS), as updated by MAP3S (5). The industrial categories for point sources are utilities, mining, paper and allied products, chemicals and allied products, petroleum refining, concrete and related products, metal industries, "other" manufacturing, and miscellaneous. The sources listed in the NEDS inventory include only those that emitted at least 250 tonnes (250,000 kg) per year of SO_x (as SO_2), NO_x (as NO_2), hydrocarbons (as

methane), or particles in 1977-1978. The sources near the sites, their distance (km) and heading (angle from the site), and their 1978 emission data are presented in Table 2-2. In addition, cities with populations greater than approximately 25,000 within 50 km of the site are listed. No data are available for soil dust, another important contamination source for precipitation chemistry. The sites are briefly described below. Features that do not conform to the selection criteria, as well as important point sources, are noted.

Uvalda, GA (Site 14)

The site is located 75 m south of a pond and 53 m northwest of a grove of pine trees. Some livestock are nearby (approximately 25 m away). No other sources are present near the site. Prevailing winds are from the west-southwest.

Lancaster, KS (Site 18)

The site is on pasture land with trees in all directions. No animals or obstructions are present. The largest sources are power plants, 43 km northeast and 37 km north-northwest. The closest emission source, 5.2 km south, is a grain storage facility and is a large source of particles. However, since the prevailing winds are from the west, this source should generally have little effect.

Underhill, VT (Site 20)

The site is in a hilly area and is about 19 km east of the town of Burlington, VT, which has a population of 38,600. The collectors are mounted on a level wooden platform. The only large source is a paper products plant, 36 km northwest, which emits hydrocarbons. There are power lines 13 m from the collector, and these do not conform to the obstruction criterion. This site has been chosen as a National Trends Network site.

Table 2-2

SOURCE EMISSIONS INVENTORY FOR SITES

Site	Emission Source	Distance (km)	Heading (degrees)	Particulates (tonnes/yr)	SOX (tonnes/yr)	NOX (tonnes/yr)	HC (tonnes/yr)
14	None						
18	Power Plant	43	61	1,700	4,000	3,500	30
18	Food & Kindred Products	15	96	300	80	100	20
18	Power Plant	37	321	50	10	1,300	100
18	Paving Mixtures & Blocks	46	152	600	0	0	0
18	Food & Kindred Products	44	62	400	0	10	0
18	Food & Kindred Products	41	65	300	0	0	0
18	Paving Mixtures & Blocks	28	26	200	0	0	0
18	Wholesale Trade-Grain	5	201	1,800	0	0	0
18	Minerals/Earth Grounding	15	96	700	0	0	0
18	Wholesale Trade-Grain	37	321	300	0	0	0
18	Wholesale Trade-Grain	28	26	300	0	0	0
18	Wholesale Trade-Grain	46	247	200	0	0	0
18	Wholesale Trade-Grain	38	191	200	0	0	0
18	No Cities						
20	Paper Products	36	332	0	0	0	400
20	Burlington, Vermont	19	258	(Pop. = 38,600)			

Sampling Period

Collocated sampling was performed at the three sites for approximately one year, as follows:

Georgia, Oct. 9, 1983 - Aug. 15, 1984
Vermont, Oct. 9, 1983 - Oct. 10, 1984
Kansas, Oct. 12, 1983 - Oct. 17, 1984

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Section 3

MEASUREMENT METHODS

This section describes the site equipment and the site and laboratory operations. The site operations include sampling procedure, shipping, and quality control. The laboratory operations discussed here include sample check-in, analysis, storage, and quality control, including analytical precision and accuracy.

SITE EQUIPMENT AND OPERATIONS

The site equipment and operations are summarized below. A more detailed description is given in the UAPSP "Field Operator Manual" (1) and the UAPSP Interim Report (2).

Equipment

Each site had the following items:

- Four automatic precipitation collectors, manufactured by Aerochem Metrics (3) (with a peaked snow roof for the Vermont site).
- One or two Universal Recording Weighing Bucket Rain Gauges (4) with an eight-day spring-powered clock and strip chart recorder. The chart is graduated in inches of rainfall and is wrapped around a vertical cylinder that rotates. An event pen marker is electrically connected to the samplers and notes the sampler lid opening and closing times on the strip chart; gauge capacity is 12 inches (30.5 cm); sensitivity is 0.02 inches (0.05 cm).
- A triple beam balance (5); capacity 2610 g, accuracy 0.1 g.

- A digital pH/temperature meter (6) and combination pH electrode (for rain or low ionic strength solutions) (7); range 0-14 pH, accuracy 0.02 pH.

- A thermistor (8); temperature accuracy 0.5°C.

- A conductivity meter (9) and dip cell (10), temperature compensated; range 0-10, 0-100, 0-1000, 0-10,000 and 0-100,000 µS/cm; accuracy 1% of full scale.

At each site, one pair of samplers was collected daily and the other pair collected weekly. Two rain gauges were installed at the Kansas and Vermont sites, while the Georgia site had one gauge.

The samplers were a modified HASL type (11) and are currently manufactured by Aerochem Metrics; they contain two 3.5-gallon plastic buckets (one for wet deposition and one for dry deposition), which are inert to inorganic constituents; a common lid, driven by a motor; and a rain sensor. When the sensor is wet, it activates a motor that moves the lid from its normal position, uncovering the wet deposition bucket and covering the dry deposition bucket. When the sensor is dry again, the lid returns over the wet bucket.

The rain gauge has a double traverse pen with a range of 0 to 6 inches on the first scale and 6 to 12 inches on the second. The gauge is readily calibrated to ±0.02 inch (±0.05 cm) except for an interval around the 6-inch level, where the calibration is good to only ±0.1 inch (±0.25 cm).

The conductivity meter is calibrated with 75 µS/cm KCl standard solution. Thus the calibration range is 0-100 µS/cm, which is used for most of the precipitation samples.

The useful life of the combination pH electrodes for precipitation samples in the UAPSP has been three months to one year, with an average of six months. The pH meter and electrode are calibrated at pH = 4.0 and 7.0 with standard buffer solutions.

Field Procedures

All operators were trained in site operations based on the U.S. EPA "Operation and Maintenance Manual for Precipitation Measurement Systems" (12) and the UAPSP "Field Operator Instruction Manual" (1). Daily site visits were generally made at about 0900 LST to check the equipment and remove any precipitation collected by the daily samplers.

Daily samples were weighed and a portion removed from each for pH and conductivity measurements. These measurements were made about an hour after sample removal from the collector to allow for temperature equilibration with the standard solutions required for meter calibration and a pH quality control check solution. When the sample was frozen or contained snow, it was allowed to thaw first, prior to removal of the aliquot for field analysis. If the rest of the sample after pH and conductivity measurement was greater than 20 g, a 500 ml sample (or whole sample if less than 500 ml) was transferred to a clean, labeled, plastic bottle and sealed; the rest of the sample was discarded. If less than 20 g, the sample was discarded and thus was lost from the weekly composite of daily results. The effect of this procedure on the comparisons with weekly samples will be discussed in Section 4.

Weekly samples were removed on Monday from the Georgia and Vermont sites and on Tuesday at the Kansas site. The same procedures were followed with the weekly samples as with the daily samples, except that the weekly samples were shipped on the day of pickup and were not refrigerated prior to shipment. However, both daily and weekly samples were shipped together to the analytical laboratory at low temperature. If no event occurred within a week, the buckets were rinsed with deionized water to remove any dust that may have deposited and then reused. A protocol to accomplish this was implemented throughout the UAPSP network (1,14). The rinse water was shipped to the central laboratory for analysis as a dynamic blank.

Each sample was identified by site, sampler, date, and weight. To prevent confusion of the sample identity, since there were four samplers at a site, the sampler buckets were inscribed with an identification number. The information was recorded both on the sample bottle and on a data sheet. Also listed on the data sheet were the site values of the pH and conductivity, the rain gauge precipitation reading(s) in inches per event, the number of lid openings, and any

pertinent observations. The data sheet thus served as a checklist to record all station data and observations.

Shipping

Daily samples were preserved by maintaining them at about 4°C in a refrigerator and using cold packs when shipping to the laboratory. The cold samples were packed directly from the refrigerator into an insulated Styrofoam box with four frozen gel packs. Weekly samples were packed together with the daily samples for cold shipment to the laboratory. The carton was shipped by air freight each week on Monday or Tuesday after packing of the weekly samples so that delivery would be made before the weekend. It generally arrived at the laboratory on Wednesday and rarely later than Friday.

Quality Control

The objectives of the quality control procedures in the field were to maximize capture of uncontaminated samples, to identify and document them, to preserve their integrity until their arrival at the laboratory, and to obtain each site's measurement of precision and accuracy of pH and conductivity. (The pH and conductivity were used to indicate if precipitation samples had degraded between the field and laboratory measurements.) All field equipment was tested in the laboratory and any problems were corrected before the equipment was sent to the field.

To minimize contamination of the samples, measurements were made on sample aliquots and never on the whole sample. In addition, periodic rinses of the sampler bucket were sent to the laboratory for analysis to yield dynamic blanks. Each operator was contacted weekly by EMSI personnel to confirm sample shipment and problems. To minimize downtime of equipment, each operator was given a schedule of tests to perform on a routine basis (1,12). Collector malfunction was evidenced by large differences in the amounts of precipitation collected by the collocated samplers or differences between the sampler and rain gauge; by the event pen markers (indicating late or premature lid opening or closing, or lid cycling); the presence of precipitation in the dry bucket after an event; and direct observation. Rain gauge problems included inoperative pens, clock malfunction, and incorrect response to calibration weights.

Each site was audited semi-annually, and the auditor inspected the site for problems. The operator was questioned and observed as he went through his routines, including a test sample measurement. Any discernible equipment malfunction was corrected, the rain gauge was recalibrated and adjusted, and operator questions and problems were addressed at this time. An audit report was written.

To help assure routine correct measurement of pH, each site was supplied with a dilute acid sample of known pH for measurement with the precipitation samples. If the measured pH of the check sample differed from the labeled value by 0.10 unit or more, it alerted the operator and the laboratory that a problem was present. A new electrode generally corrected the problem.

To evaluate the site's precision and accuracy for pH and conductivity, test solutions were sent monthly to the stations for analysis; the chemistry of the test solutions was unknown to the site operator. These are not true environmental precision and accuracy results since the test solutions were not precipitation samples but consisted of dilute acid plus salt solutions with rain-type pH and conductivity values.

The test solutions were prepared at the EMSI laboratory, and the pH and conductivity of each sample were measured just before the sample was sent to the field. For calculating accuracy the EMSI measurements were assumed to be the standard. Station operators took readings on five aliquots of the solution, reported the values to the laboratory, and returned the remainder of the sample. After their return to the laboratory, the samples were remeasured for pH and conductivity to assure that they had not degraded. If the laboratory measurements after the sample's return matched those before shipment to the field (within 0.1 pH unit and 10% in conductivity), the samples were assumed to be stable; if not, the measurements were not used to assess precision and accuracy.

Accuracy is based on the absolute difference between the average field value and the average laboratory value. Field precision for pH and conductivity is obtained from the standard deviation of the measurements made on the five aliquots of each sample. Generally, the standard deviation for a well-performing electrode is less than 0.05 pH unit, and for conductivity less than 2 μS/cm.

The average accuracy for pH at the Georgia, Kansas and Vermont sites was respectively 0.08, 0.17 and 0.05 pH units and for specific conductance 8.7%, 13.3%, and 3.0%. The poor accuracy in pH for the Kansas site was due to two bad electrodes, which were subsequently replaced. The precision for pH for the Georgia, Kansas, and Vermont sites was respectively 0.02, 0.04, and 0.05, and less than 1 μS/cm for conductivity.

LABORATORY OPERATIONS

The laboratory operations are summarized below. A more complete discussion is given in the UAPSP Interim Report (2) and in the "Laboratory Standard Operating Procedures Manual" (13).

Sample Check In

When a sample arrived at the laboratory, the temperature of the box interior was measured. Each sample was logged in, and the temperature and any pertinent codes were recorded on the data sheets. Approximately every twentieth sample was marked for analysis in duplicate as a quality control measure. All the samples were assigned consecutive EMSI laboratory numbers and the chemist performing the analysis in the laboratory had no awareness of either the collection schedule or the identity of the collocated samples.

Analyses

If sufficient sample (over 30 ml) was present, the following order of analysis was taken to minimize chance of degradation:

pH, conductivity;

NH_4^+;

$SO_4^=$, NO_3^-, Cl^-;

Ca^{2+}, Mg^{2+}, Na^+, K^+.

The pH and conductivity were measured within one week of receiving the sample. Other observables were analyzed as the instruments became available, generally within six weeks.

If insufficient sample was available for complete analysis, the order of analysis followed the importance of the constituents. The priority and the required volume for analysis were:

pH, conductivity (10 ml)

$SO_4^=$, NO_3^-, Cl^- (5 ml);

NH_4^+ (3 ml);

Ca^{2+}, Mg^{2+}, Na^+, K^+ (6 ml).

All samples were analyzed without filtration. Filtration has the advantage of removing both bacteria, which can degrade nitrogen and phosphorus compounds as well as organic acids, and soil particles, which are generally basic and react with hydrogen ion. However, filtration has the disadvantage of being a source of contamination and is costly. To minimize degradation, the samples were kept cold after removal from the collector, during shipment, and before and after analysis at the laboratory. In addition, portions of the sample that were removed for analysis were decanted to eliminate sedimented particles.

The methods of analysis and their detection limits are given in the first columns of Table 3-1. For most analytes the detection limit is equal to twice the standard deviation of the baseline noise. For those analytes for which responses are read from a strip chart (NH_4^+, $SO_4^=$, NO_3^-, and Cl^-), there is no real measure of baseline noise, and the concentration corresponding to twice the baseline penwidth was used as the detection limit.

Sample Storage

The samples, when not being analyzed, were stored in a refrigerator at 4°C. After all the analyses were completed, the remaining sample, if larger than 100 ml, was stored at 4°C for one year for possible reanalysis at some later date.

Table 3-1

EMSI LABORATORY METHODS, DETECTION LIMITS, PRECISION AND ACCURACY FOR PRECIPITATION SAMPLE ANALYSES

			Precision (mg/l)			Recovery (%)		
Method	Analyte	Detection Limit (mg/l)	N	RMSD[a]	Conc. at 10% CV[b]	N	Range of Standard (mg/l)	Mean ± SE[c]
pH meter	pH	---	150	0.013[d]	---	---	---	---
Ion chromatography	$SO_4^{=}$	0.020	150	0.029	0.040	32	<1.0	100.0 ± 0.4[e]
						346	1.0 - 10.0	101.0 ± 0.1
	NO_3^-	0.020	145	0.027	0.025	18	<1.0	101.2 ± 0.6
						329	1.0 - 10.0	101.2 ± 0.1
	Cl^-	0.002	134	0.010	0.010	20	<0.2	102.7 ± 0.8
						345	0.2 - 2.0	101.1 ± 0.2
Automated colorimetry	NH_4^+	0.010	112	0.0054	0.025	43	<0.5	100.4 ± 0.3
						246	0.5 - 5.0	99.4 ± 0.1
Atomic Absorption	Na^+	0.001	105	0.0022	0.025	405	<1.0	99.4 ± 0.1
	K^+	0.010	111	0.0024	0.025	413	<1.0	99.5 ± 0.1
	Ca^{2+}	0.020	126	0.0042	0.025	402	<1.0	100.7 ± 0.1
	Mg^{2+}	0.002	123	0.0007	0.005	388	<0.2	99.7 ± 0.1
						17	0.2-2.0	100.7 + 0.2

(a) From 1983-1984 data for split samples

$$\text{Root Mean Square Deviation} = \left[\sum_{i=1}^{N}(X_{1i} - X_{2i})^2/2N\right]^{1/2}$$

where X_{1i} and X_{2i} are the duplicate analyses and N is the number of sample pairs.

(b) CV = coefficient of variation

(c) Standard error of the mean = $\left[\sum_{i=1}^{N}(R - \bar{R})^2/N(N-1)\right]^{1/2}$

(d) pH units

The reanalysis of "old samples" and comparison of results for analytical consistency are a feature of the quality control system employed in the EMSI laboratory (14).

Quality Control

All analytical instruments were calibrated at least once a day. In addition, reagent blanks, and split samples were analyzed daily. Instrument response was sent directly to the computer for many of the analyses, thus eliminating errors in transcription of data. When data were input to the computer manually, double entry was used. A full description of the quality control program implemented for UAPSP by EMSI is provided elsewhere (14).

Analytical Precision

The tolerance bounds of the laboratory data are measured by their precision. Precision is derived from the data for duplicate or split (not collocated) sample analyses. The precision is calculated from the equation for root mean square deviation:

$$\text{Root Mean Square Deviation} = \left[\sum_{i=1}^{N} (X_{1i} - X_{2i})^2/2N\right]^{1/2}$$

where X_{1i} and X_{2i} are the duplicate analysis values of the ith sample. The laboratory results for over 100 split samples analyzed in 1983 and 1984 are shown in Table 3-1. The precision values in Table 3-1 are generally similar to or better than those found in the 1979-1980 SURE study (15). Since the measurement error increases with concentration, the coefficient of variation (the ratio of the standard deviation to the mean concentration) is generally a more meaningful value. The coefficient of variation, CV, is much more constant than the mean or standard deviation over large concentration ranges, but generally increases rapidly with decreasing concentration below a certain level. The concentration levels below which the CV increases above 10% are shown in Table 3-1. Concentrations equal to or greater than these levels can be determined with good precision, whereas the relative uncertainty for concentrations below these values is

large. Thus the 10% CV concentration is the limiting concentration for attaining good analytical precision.

Analytical Accuracy

Laboratory accuracy was assessed by analyzing prepared samples of known concentration. The concentrations of these laboratory standards was unknown by the laboratory technician. Accuracy is measured as percent recovery, defined as the percent ratio of the measured concentration to the true standard concentration. A variety of laboratory standards were prepared across a range of concentrations for each constituent.

The accuracy results are presented in Table 3-1. For one or two concentration ranges for each analyte, the table lists the mean percent recovery and the standard error about the mean. The means range from a minimum of 99.4 to a maximum of 102.7 percent recovery. For those analytes where two ranges of standards were prepared, the percent recovery values are generally more variable in the more dilute solutions, as would be expected. The mean recovery values are similar to those reported for the SURE data (15).

In 1983-1984 EMSI was involved in five interlaboratory comparison tests with Research Triangle Institute (RTI). The RTI results, which are presented in its quality assurance reports (16), generally showed agreement to within 5% for ions between the two laboratories. Other laboratory quality controls include use of the computer to automatically flag the following conditions: spike data out of control, below-detection-limit data, calibration constants out of tolerance, and inconsistencies in precipitation collection amounts, in cation-anion equivalents, and in measured versus calculated conductivities.

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Section 4

DATA MANAGEMENT AND STATISTICAL METHODS

This section describes data management procedures pertinent to data quality control, screening for rejection of outliers, data processing, and statistical testing.

QUALITY CONTROL SCREENING

Study data were invalidated for the following reasons:

- Obvious physical contamination of a sample
- Instrument malfunction
- Evidence of erroneous data entry

Obvious physical contamination of samples was indicated on the field sheets by the site operators, verified by the receiving clerk at EMSI, and the appropriate code entered into the data base. The contaminated samples were not analyzed. A code was also entered in the data base for documented instrument malfunctions indicated by the site operator. The various codes and data flags utilized in the data base have been documented (1) and all data sheets are archived in bound notebooks by site and date.

A double entry procedure with 100 percent verification was used for all data manually entered into the computer. In this procedure, computer-generated outputs document the differences, if any, between the two corresponding entries. All discrepancies are resolved before the data are permanently recorded in the data base. Laboratory chemists manually check approxiately 5 percent of all data, concentrating on extreme observations of concentrations and ion balance

data, thus verifying both instrument calibration and the integrity of the analytical process. On the basis of these checks some samples were reanalyzed and the results reentered into the data base. No extreme observations were deleted from the main data base if they passed all the checks described here. For the purpose of this study, values below detection limits were set equal to zero. Further details on data handling and validation can be found in other EPRI reports (2, 3).

DATA PROCESSING

The collocated sampler data were used to determine random measurement error (precision), mean and median concentrations of daily and weekly sampling, and the bias between the measured weekly and the derived weekly values, composited from the corresponding daily results. All derived weekly concentrations were calculated separately for each collector from the daily values as the precipitation-weighted mean, $\bar{C} = (\Sigma_i\ C_i P_i)/(\Sigma_i\ P_i)$, where C_i and P_i are the daily concentration and sample weight. The weekly precipitation values were derived from the sum of the daily precipitation weights for the week for each collector. The weekly deposition values were calculated from the product of the measured weekly concentration for each collector and the total daily precipitation depths from the rain gauge, i.e., $D = 10 C_w\ \Sigma_i\ R_i$, where C_w is the weekly measured concentration in mg/l, and R_i is the daily rain gauge depth reading in cm. The derived weekly values were calculated from the total of the daily deposition values, i.e., $D = 10\ \Sigma_i\ C_i R_i$. Annual deposition values were calculated by summing the weekly deposition values.

The data were classified by sampling site, precipitation type (rain, snow, or mixed: rain + snow + ice), and by meteorological season (spring -- March-May; summer -- June-August; fall -- September-November; and winter -- December-February). A weekly sample that consisted of one or more rain events and one or more snow events was classified as mixed.

Only events having a rain gauge depth greater than 0.51 mm (0.02 inch) were included in this study to ensure that a sufficient sample was available for analysis. Thirteen daily events with such low-volume precipitation were not analyzed. At the Georgia site there were two weeks with one low-volume event each; each events represented less than four percent of the total precipitation

for the week. There was only one low-volume event at the Kansas site; in the week of this event there were two other events and the low-volume event represented 12 percent of the total weekly precipitation. Most of the low-volume events occurred at the Vermont site, where there were 10 such events in seven weekly periods. For five of those weeks, the one or two low-volume events represented less than three percent of the total weekly precipitation. In one week there were four snow or mixed events, one of which was a low-volume snow event representing 15 percent of the total precipitation. One week in late June had four rain events, three of which were low volume; the fourth event that week was small, and the three low-volume events accounted for 11 percent of the weekly precipitation. For the Georgia and Kansas sites the very small number of low-volume events would not be likely to bias the method comparison results. For the Vermont site, where the majority of low-volume events occur (13 percent of the weeks at the Vermont site have one or more low-volume events), there may be a bias in the weekly concentrations derived from the daily events, especially if such small precipitation events have unusually high concentrations. Further investigation of possible effects of low-volume events in Vermont on the comparison of weekly versus daily methods is beyond the scope of the present study.

There were also low-volume samples with precipitation amounts greater than 0.51 mm but not enough for complete chemical analysis, which required 24 ml of sample. As indicated in Section 3, a prescribed order of analysis was followed. At a minimum, pH and conductivity were measured; this required 10 ml of sample. If an additional 5 ml was available (i.e., total sample volume at least 15 ml), the anions ($SO_4^=$, NO_3^-, and Cl^-) were analyzed next. Ammonium was next, requiring 3 ml (total sample volume at least 18 ml).

Measurements are missing, then, if there was a sample less than 24 ml. There are also missing samples if a sampler was malfunctioning. In addition, samples with visible organic material contamination (e.g., bird droppings) were considered invalid and are not used in the analysis. For weeks containing one or more missing daily samples having a rain gauge depth greater than 0.51 mm, a derived weekly sample was not calculated.

The distributions of collocated differences in the daily and weekly data for the three sites and for the three precipitation types are roughly symmetric with long tails. Outliers contain important information about the measurement process, but can also be the result of errors or unusual events extrinsic to the measurement

process, such as contaminations. A small fraction of data are in the tails and their elimination removes their disproportionately large influence on testing for statistical significance of observed differences using parametric methods. In this study, outliers were identified as those collocated differences beyond three standard deviations from the mean for each observable. Collocated sample pairs were considered outliers if one or more of the following criteria were met:

(a) One of the four major ion differences (H^+, $SO_4^=$, NO_3^-, and NH_4^+) of that sample pair was outside the 3σ acceptance limits,

(b) At least three of the minor ion differences of the pair were outside the acceptance limits,

(c) One of the minor ion differences of the pair was outside the 3σ acceptance limits, and three out of the four primary ions for the same sample were at either extreme of the collocated pair distribution.

Thus, all or none of the ion measurements in a collocated pair are considered to be outliers. Outliers in collocated differences of precipitation mass (determined by weighing the Aerochem Metrics buckets) were identified separately. Collocated precipitation differences were considered outliers if they were beyond three standard deviations of the mean collocated difference.

A screened data set was created after removal of outliers. If a weekly sample was identified as an outlier, it was discarded for the screened data set. However, if a daily sample identified as an outlier represented less than 20 percent of the total precipitation mass for the week, then the sample was used to calculate a derived weekly value, but was not used to calculate bias and precision of the daily data. If a daily sample was identified as an outlier and it represented more than 20 percent of the total precipitation mass for the week, then no derived weekly value was calculated for the screened data set, and the sample was not used to calculate daily sampler bias and precision. This procedure resulted in a screened data set with the following numbers of samples:

	Daily		Measured Weekly	
	Unscreened	Screened	Unscreened	Screened
Georgia	67	63 (94%)	35	33 (94%)
Kansas	86	72 (84%)	38	37 (97%)
Vermont	142	133 (94%)	52	47 (90%)

In both the screened and the unscreened data sets, when one of two paired samples was missing or rejected as an outlier, no collocated difference was obtained. However, the valid collocated measurement was taken as the mean for the pair.

For the parametric statistical tests, which are based on assumptions of normality of the distributions, the reduced data set (outliers removed) was used. Nonparametric techniques are used to test the significance of the observed differences, and since they are relatively insensitive to the data in the tails of the distribution, the complete data set (i.e., including outliers) was used for these analyses. Outliers were deleted for the parametric statistical analyses so they do not exert undue influence on the results; where possible, however, nonparametric methods were applied to the unscreened data set. There are alternative methods for identifying outliers and for statistical analysis of data sets containing outliers. For example, rather than rejecting all ions together or none at all, one could delete only those measurements corresponding to collocated differences beyond three standard deviations from the mean for the appropriate distribution. One could also use a more robust estimate of scale other than the sample standard deviation (which is disproportionately affected by outliers); acceptance limits can then be based on the robust scale estimates. One example of a robust scale estimate is the sample interquartile range, which is the difference between the 75th and the 25th percentiles of the sample distribution.

An alternative to nonparametric techniques or to deleting outliers before applying parametric techniques is to use statistical techniques that accommodate outliers. These techniques, which have been developed mostly within the last 10 years, are known as robust/resistant methods. They do not depend upon assumptions of normality and are not heavily influenced by outliers, yet they have much greater power than standard nonparametric techniques. The book edited by Hoaglin, Mosteller, and Tukey (4) is a good reference for these procedures. Although robust/resistant procedures are powerful and applicable in a wide variety of situations, they can be computationally intensive and have not yet come into general use outside the statistical community.

STATISTICAL TESTING

Preliminary evaluation of the analyte data for collocated concentration differences showed that the distributions appeared to be symmetric but not normally distributed as demonstrated in Section 5 (Figures 5-2 through 5-7). The distributions of weekly derived minus weekly measured concentration data showed similar behavior (Figures 5-10 through 5-12). These plots show distributions with outliers in both the upper and the lower portions. Because the distributions are not skewed (i.e., outliers in one half of the distribution only), no monotone transformation can be applied to make the distributions more normal.

Although the design of the study would suggest that the statistical analysis proceed with a nested (random effects) analysis of variance model, this model was not applied because of the reliance on assumptions of normality, which are not met. Instead, a nonparametric Wilcoxon signed-rank test was used to evaluate the statistical significance of differences in paired data. For example, suppose there appears to be a systematic difference between measured and derived weekly concentrations at the same site. The Wilcoxon test is used to test the significance of this apparent method bias. The measured and derived concentrations for a given week and site form a pair. The difference between each pair of numbers is calculated, and the absolute differences are ranked. The Wilcoxon statistic is the sum of the ranks of the positive differences minus the sum of the ranks of the negative differences. If there were no systematic difference, positive and negative differences would be about equal in number and of about the same size, and the rank-sum would be near zero. A large, positive rank-sum indicates that either (1) more differences are positive, or (2) the positive ones are larger, or (3) both, i.e., a systematic positive difference. Similarly, a highly negative rank-sum indicates a systematic negative difference.

The influence of outliers is limited by the use of ranks instead of raw data in the Wilcoxon test. Large differences still count more than small ones, however, because they have bigger ranks. The probability of the Wilcoxon indicating a significant difference when there is no real difference is independent of any distributional assumptions. The probability of the Wilcoxon test correctly indicating a small, real difference is not much less than with the t-test for normal distributions and much greater for some outlier-prone distributions. Throughout this study, a significance level of $\alpha = 0.05$ was used.

Several robust parametric tests available from the BMDP statistical routines developed by the University of California (5), were also used in the data analyses. These included testing for the equality of the means of the collocated pair averages and collocated pair differences among the sites for all analytes. For parametric tests, in general, establishing levels of significance for the equality of the mean observations at each site is strongly dependent on the normality of the parent population from which the data are drawn and the equality of the variances of the distributions. To overcome the latter difficulty, the Levene Test (6), a robust test of the equality of variances, was used. Welch's test is used for certain problems in one-way analysis of variance. For example, are there significant differences in method bias (i.e., daily versus weekly collection protocols) from site to site? As in the usual F-test, a (weighted) variance of the estimated biases for the three sites is divided by an estimate of what it would be if there were no difference. However, the usual assumption of equal variances within groups (sites) is obviated by not pooling the variances and using a generalization of Satterthwaite's approximation to the degrees of freedom (5).

The precision of measurements for paired samplers is estimated two ways: pooled standard deviation and median absolute collocated difference. The pooled standard deviation is

$$S_p = \left(\sum_{i=1}^{N} d_i^2 / 2N \right)^{1/2}$$

where the d_i are the pair differences and N is the number of pairs. This estimate of precision includes variability both in the chemical measurements and in the samplers (i.e., sampler bias), both of which are random errors that cannot be controlled. This is a standard calculation (sometimes known as Youden's method) and thus the results can be compared with other studies that use the same measure of precision. Furthermore, precision so defined has a direct relationship to the usefulness of the data in detecting trends if linear methods (t-tests) are used to test for trends. That is, if daily data have a pooled standard deviation half that of weekly data, then a study with daily data would be able to detect a trend of half the magnitude of the smallest trend that could be detected with the same number of weekly samples. Of course, this approach makes no allowance for the fact that there will probably be more daily than weekly samples.

On the other hand, the pooled standard deviation is very sensitive to outliers and therefore to the method chosen to eliminate outliers. This fact makes comparison across studies meaningless unless the same outlier-deletion protocols are used, which is very unlikely. Furthermore, the presence of extreme outliers suggests that linear methods may not be the best way to test for trends anyway, so that the relationship between pooled standard deviation and the sensitivity of the t-test may be irrelevant.

The other precision statistic used is the median of the absolute values of the collocated paired differences (MACD), which is not sensitive to outliers. Thus, comparison with previous daily collocation studies, such as EPRI-SURE (2) and UAPSP (3), and other studies reporting median absolute differences is straightforward. The MACD, like the pooled standard deviation, is an estimate of the variability of the distribution of differences, and thus can also be used to compare daily and weekly sampling protocols in the ability to detect long-term trends.

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Section 5

RESULTS

In this section we present the results of the statistical comparison of the daily and weekly precipitation samples. First, the frequency and types of rainfall events are described. Second, the collection efficiencies of the two sampling methods are compared. Then, the precision of the measurements (determined from collocated samplers) is discussed, with particular attention to differences between daily and weekly sampling in their ability to detect long-term trends. Next, measured and derived weekly concentrations are compared; method bias is examined by precipitation type, site, and season. Finally, seasonal and annual depositions calculated from the daily and weekly measurements are compared.

FREQUENCY OF RAIN EVENTS

The number of events at each site for each week during the study period is shown in Figure 5-1. The total number of rain events is 67 in Georgia, 86 in Kansas, and 142 in Vermont. Although the Vermont site has the largest number of rain events, the average rainfall amount in each event is the lowest among the three sites. Table 5-1 shows the distribution of precipitation types at each site. At the Georgia site there are no snow or mixed events; at the Kansas site events are predominantly rain; at the Vermont site about 40 percent of the events are snow or snow mixed with rain.

Table 5-1

FREQUENCY OF PRECIPITATION TYPES AT EACH SITE

	Precipitation Type			
Site	Rain	Snow	Mixed	Total
Georgia	67	0	0	67
Kansas	72	3	11	86
Vermont	88	29	25	142

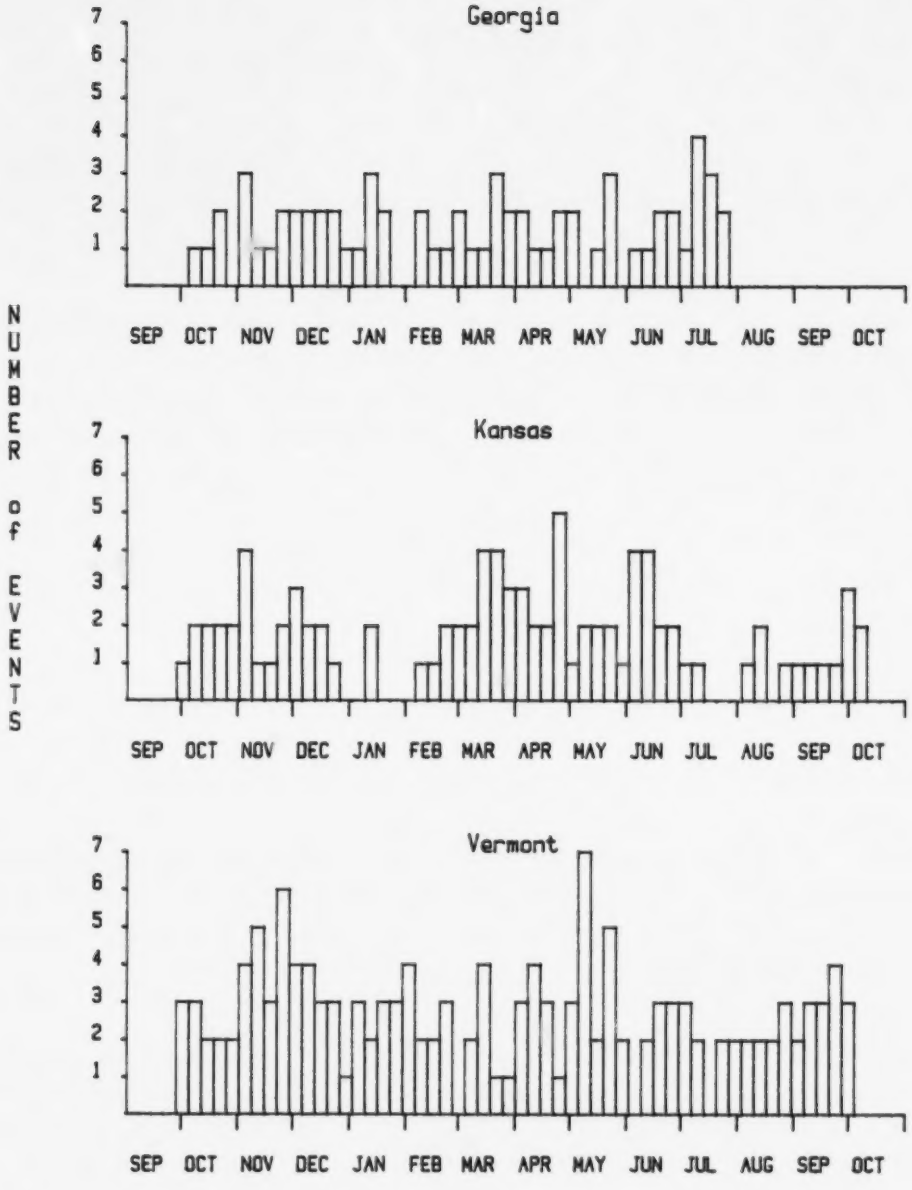

FIGURE 5-1. Frequency of rain events by week for the 1983 to 1984 study period.

COLLECTION EFFICIENCIES

Sampler performance is measured by the precipitation collection efficiency, which is the ratio of the average sample depths of the collocated buckets to the standard rain gauge depth; i.e.,

$$C.E. = \text{sampler depth/rain gauge depth}$$

for each event. The sampler depth is derived from the sample weight and the area of the sampler bucket, and the rain gauge depth is read directly from the rain gauge stripchart. The daily and weekly mean collection efficiencies for rain, snow and mixed samples for the three sites are presented in Table 5-2. Also included are the standard error of the mean and the number of samples in each category.

The mean collection efficiencies for rain events are higher than the mean collection efficiencies for snow and mixed events, which are relatively similar. This is as expected since the sampler sensor does not respond readily to dry snow, and snow capture losses also occur either when snow blows past the bucket or is blown out by wind. Collection efficiency is especially low for Kansas snow and mixed events; this may be due to drier snow or windier conditions at this site than at the Vermont site. The mean collection efficiencies for rain, which are slightly larger than unity, indicate that the samplers collect more precipitation than the gauges, possibly due to precipitation splashing off the moveable bucket lid.

The collection efficiencies for the daily and weekly mean values show little difference. The only large difference is for Vermont rain samples; the mean collection efficiency is significantly higher in the daily samples than in the weekly samples. Since the daily and weekly sample depths are both referenced to the same rain gauge, it appears that some precipitation is lost from the weekly samplers. This difference is hard to explain by evaporation alone; it might be due to different threshold sensitivities of the lid sensors, or slightly different bucket dimensions. Note that for Kansas there are four daily snow events, which correspond exactly to the four weekly samples; the lower mean collection efficiency for the weekly samples indicates a different sensor response, possibly due to evaporation and/or blow-away.

Table 5-2

AVERAGE COLLECTION EFFICIENCY FOR RAIN, SNOW AND MIXED (RAIN & SNOW) SAMPLES AT THREE MONITORING SITES

Precipitation Type	Daily Sampling			Weekly Sampling		
	Mean Coll. Eff.	SEM[a]	N	Coll. Eff.	SEM[a]	N
			Uvalda, GA			
Rain	1.059	0.021	61	1.063	0.040	33
Mixed	---	---	0	---	---	0
Snow	---	---	0	---	---	0
			Lancaster, KS			
Rain	1.090	0.033	60	1.103	0.045	24
Mixed	0.770	0.078	8	0.831	0.072	9
Snow	0.736	0.079	4	0.607	0.170	4
			Underhill, VT			
Rain	1.164	0.032	74	0.999	0.033	26
Mixed	0.948	0.066	24	0.939	0.029	17
Snow	0.943	0.060	25	0.970	0.040	4

(a) SEM = standard error of the mean = SD/√N.

COMPARISON OF DAILY AND WEEKLY CONCENTRATION MEASUREMENT PRECISION

Sampler Bias

The distributions of the daily and weekly collocated differences for precipitation mass and the concentrations of major ions (H^+, $SO_4^=$, NO_3^-, NH_4^+, and Ca^{2+}) are shown in Figures 5-2 to 5-7 for each site. In these figures the extreme bars contain all the data at the given abscissa value and beyond, and the curve represents the Gaussian distribution that has the same mean and standard deviation as the data. The means and standard deviations of the pair differences are shown in Table 5-3 as a percentage of the mean measurement. The pair differences were tested for systematic error (sampler bias) using the Wilcoxon signed-ranks test (1). Statistically significant bias between paired daily or weekly samplers is denoted in the tables with a W superscript. The same set of statistics for daily and weekly samples of each precipitation type are listed in Appendix A (Tables A-1, A-2, and A-3 for rain, snow, and mixed samples, respectively).

Most of the relative differences are below 7 percent. For daily sampling the significant differences in paired samples were as follows: precipitation amounts for all three sites; sulfate, nitrate, sodium, and chloride for Uvalda, Georgia; and ammonium for Lancaster, Kansas.

The bias for all the observables at the Georgia site, though statistically significant, is small (under 3 percent). The larger analyte concentrations, together with the larger precipitation amounts found in the same sampler, could be explained if this sampler opened sooner and captured more of the initial precipitation, which generally contains more wash-out of constituents. Concentrations of sodium and chloride could be increased by human contamination, but it is difficult to account for differential contamination between paired samplers. The larger precipitation amount in this sampler argues against evaporation as the cause of the higher concentrations. The ammonium bias for Kansas is 7.6 percent, which suggests some contamination or biodegradation has occurred.

For weekly sampling, statistically significant sampler biases were found for precipitation at the Kansas and Vermont sites, and for nitrate at the Vermont site. The precipitation biases, though statistically significant, are small,

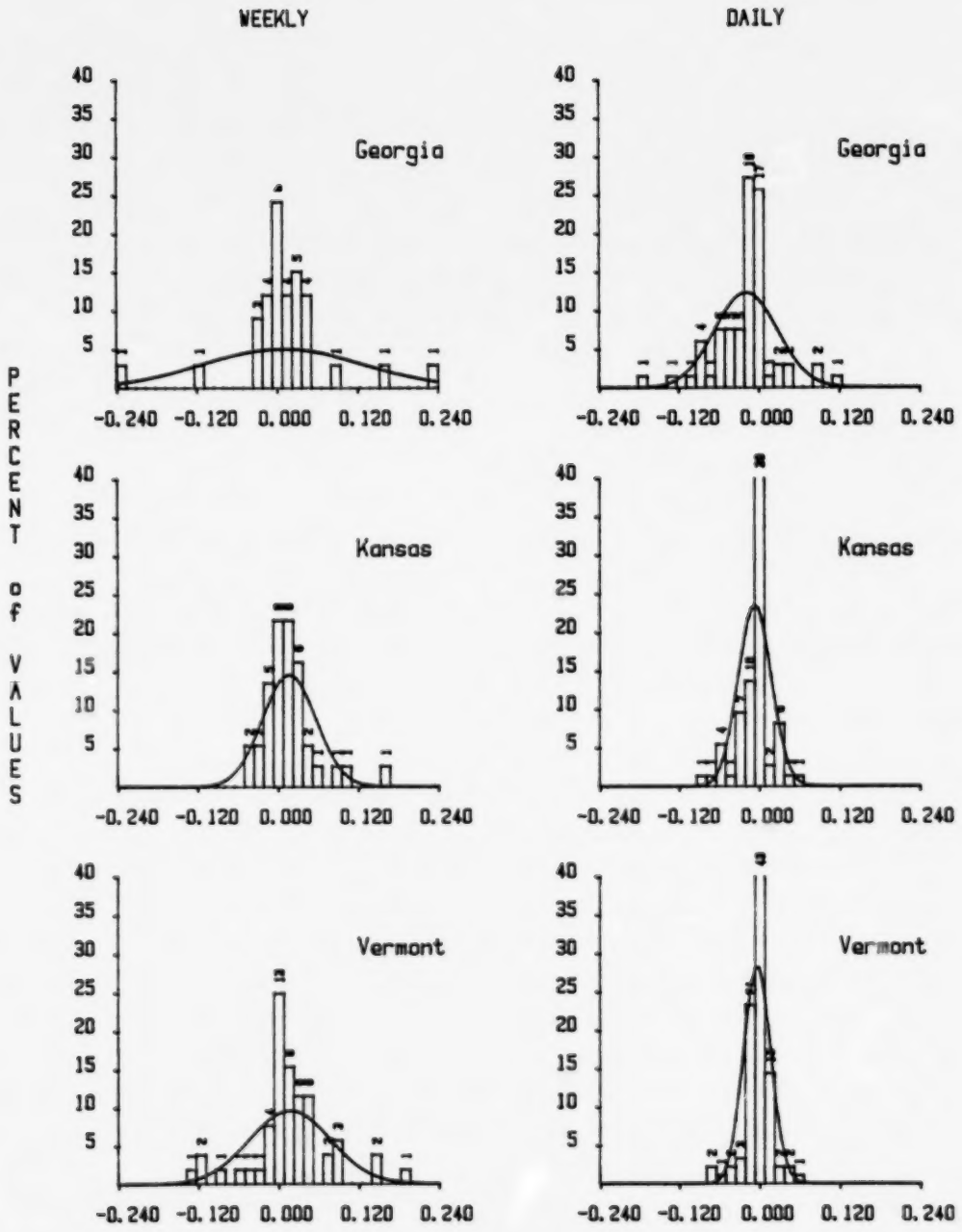

FIGURE 5-2. Distributions of collocated differences for precipitation mass in kg. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent the values at the given abscissa and beyond.

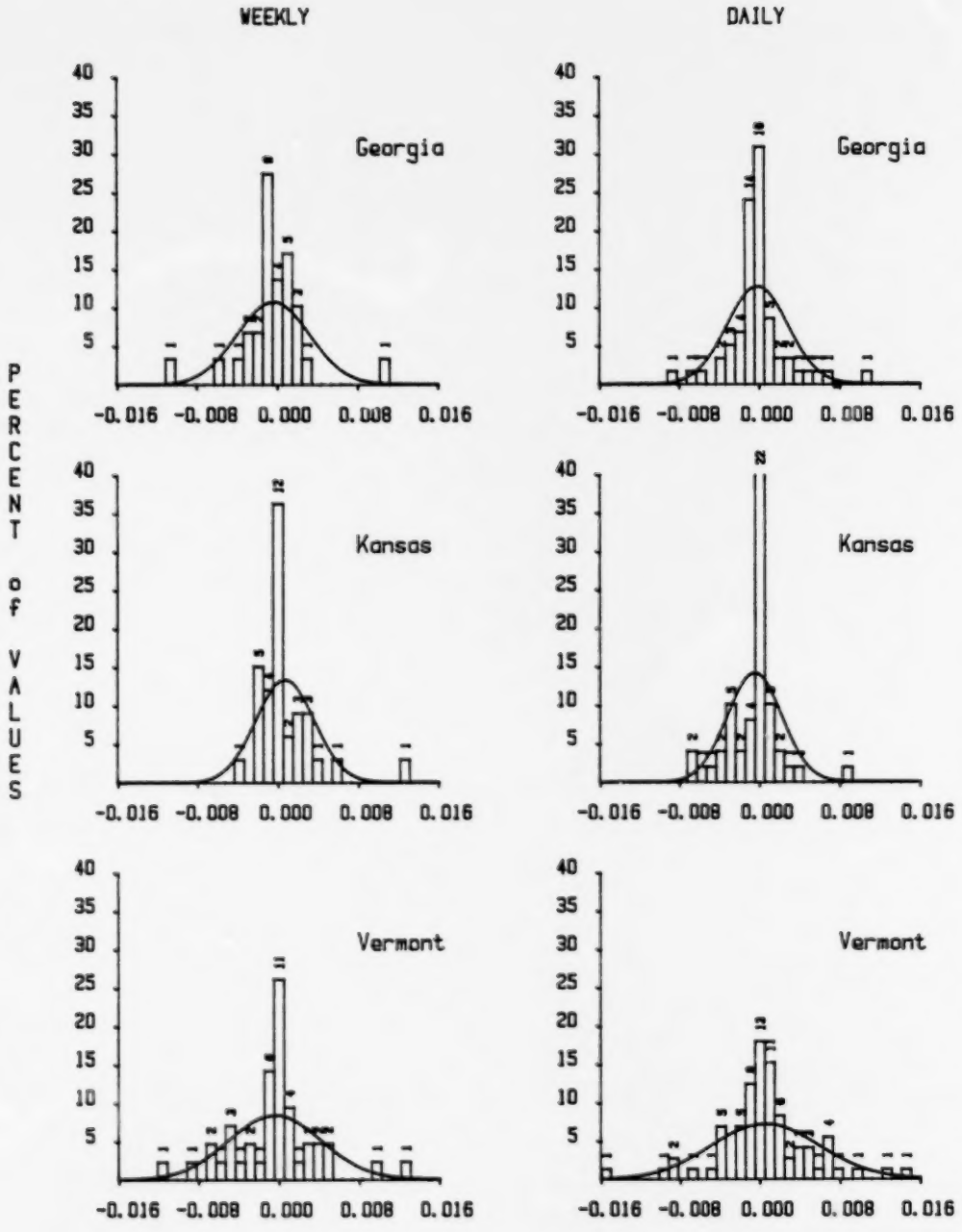

FIGURE 5-3. Distributions of collocated differences for hydrogen in mg/l. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent the values at the given abscissa and beyond.

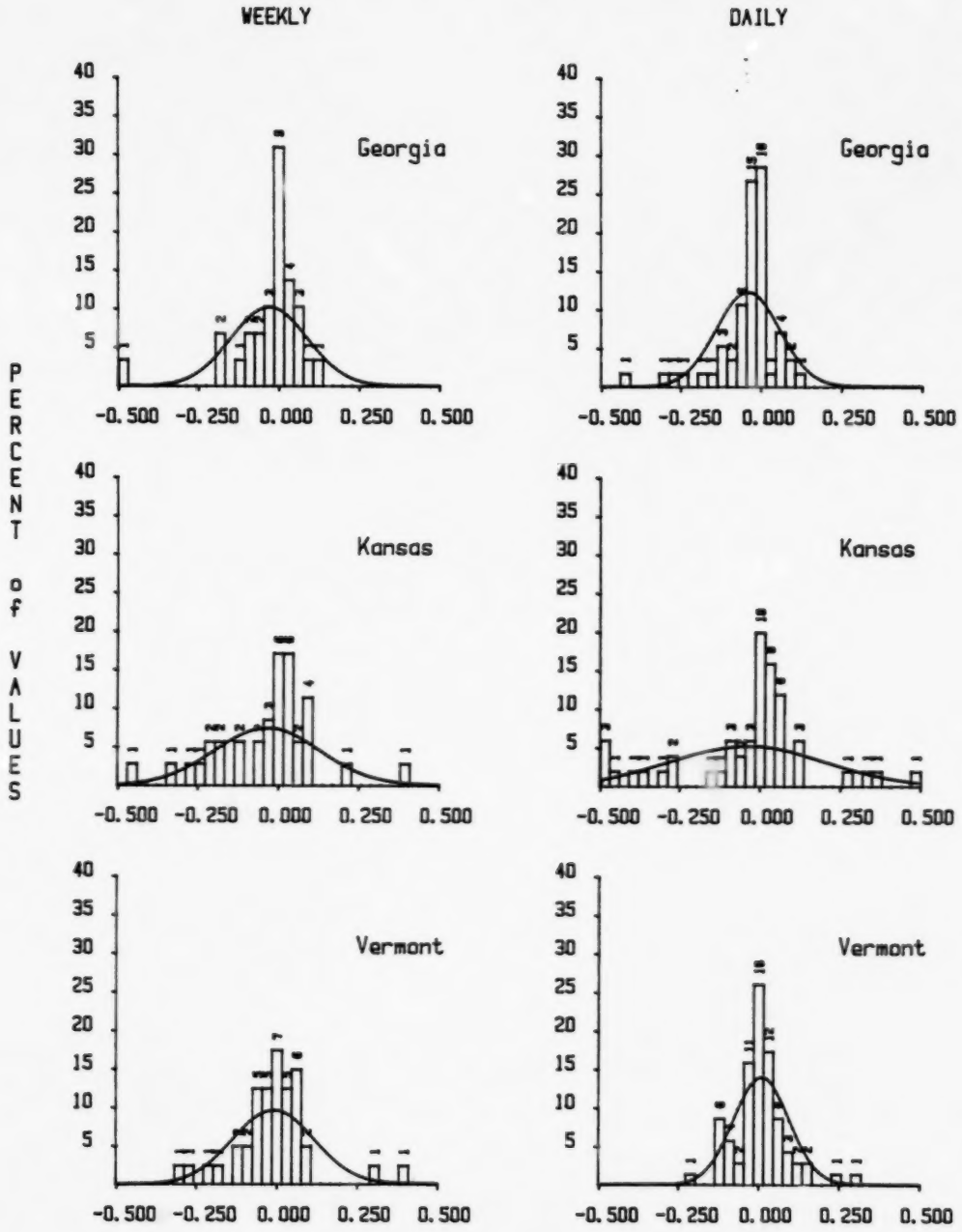

FIGURE 5-4. Disbributions of collocated differences for sulfate in mg/l. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent the values at the given abscissa and beyond.

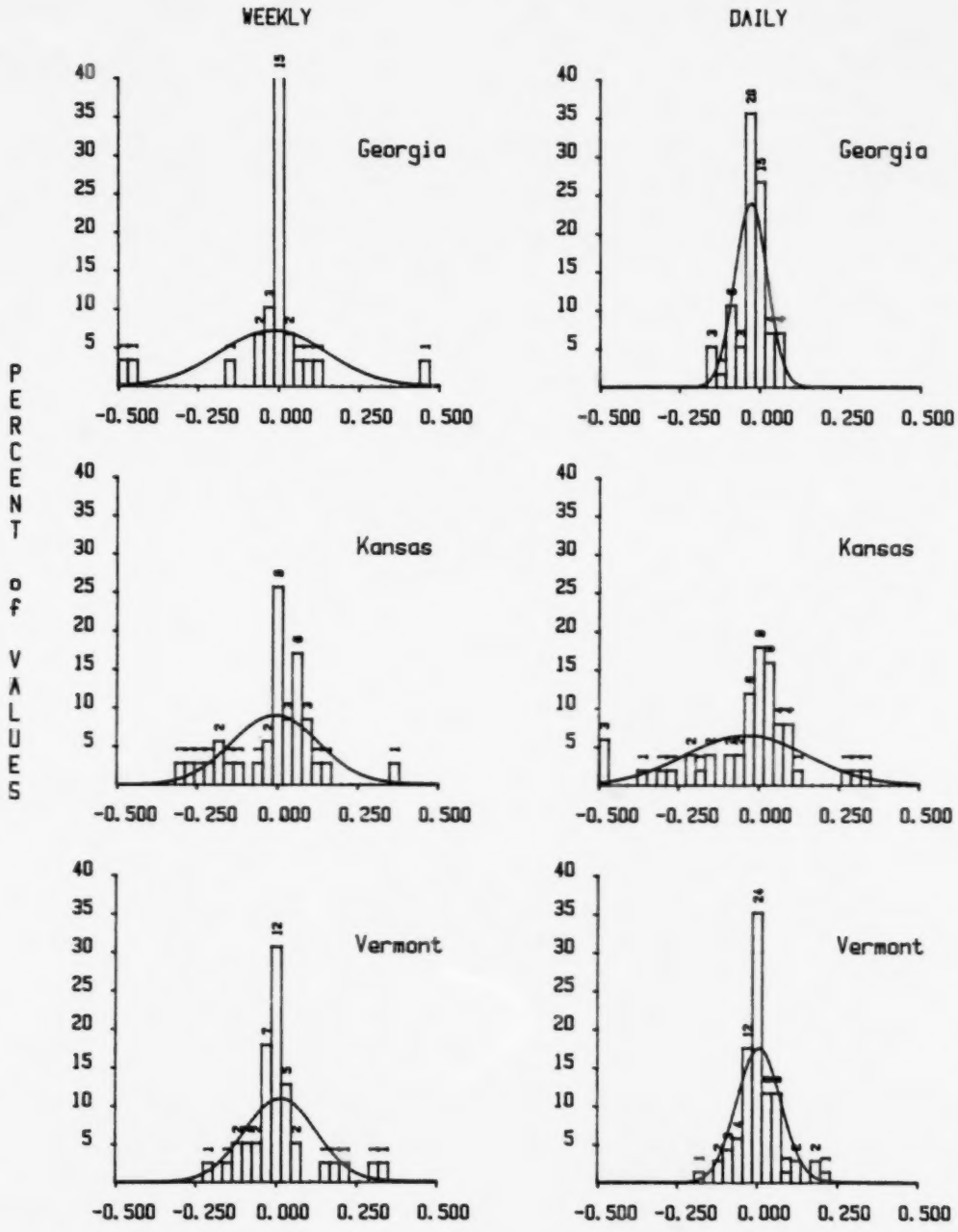

FIGURE 5-5. Distributions of collocated differences for nitrate in mg/l. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent the values at the given abscissa and beyond.

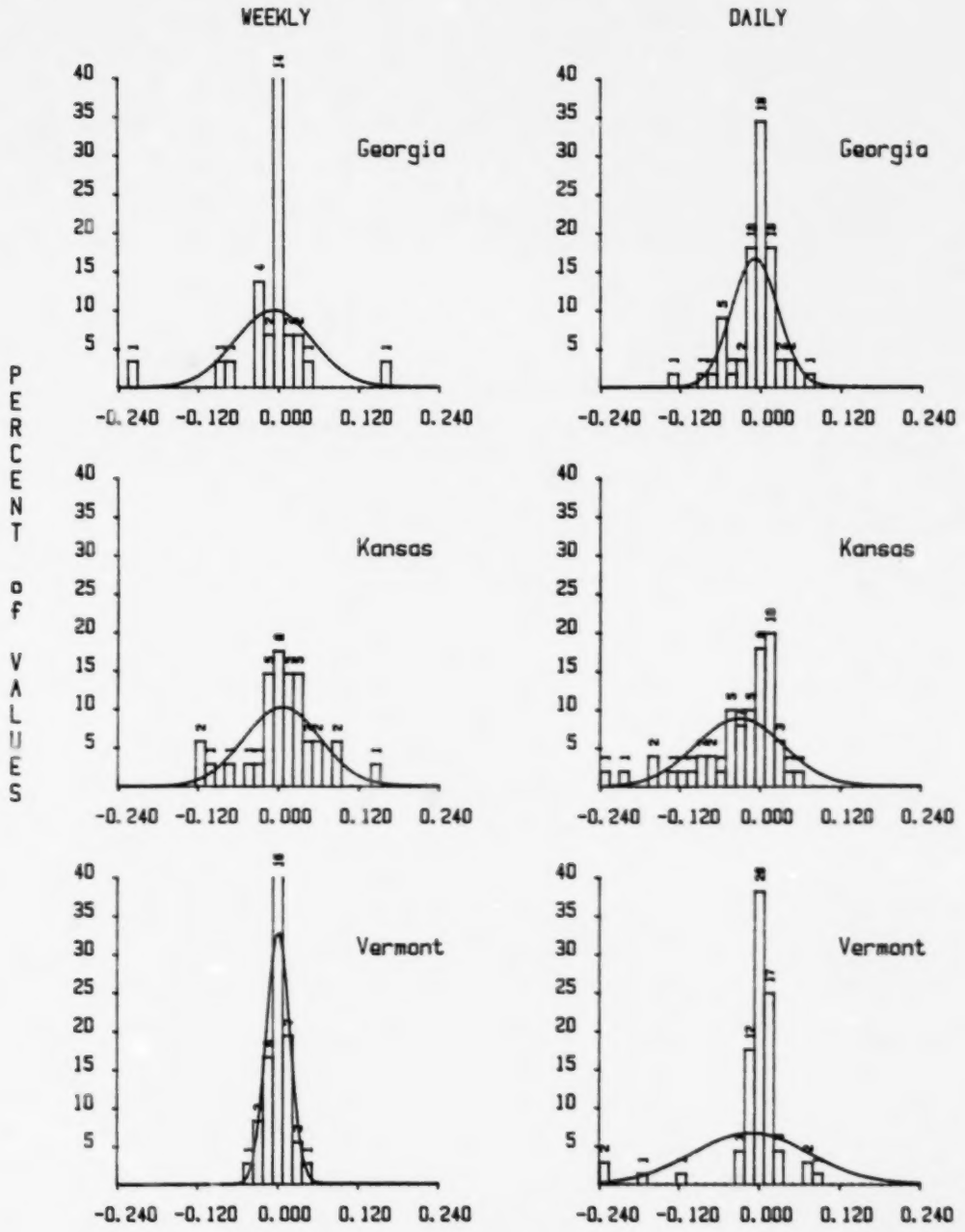

FIGURE 5-6. Distributions of collocated differences for ammonium in mg/l. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent the values at the given abscissa and beyond.

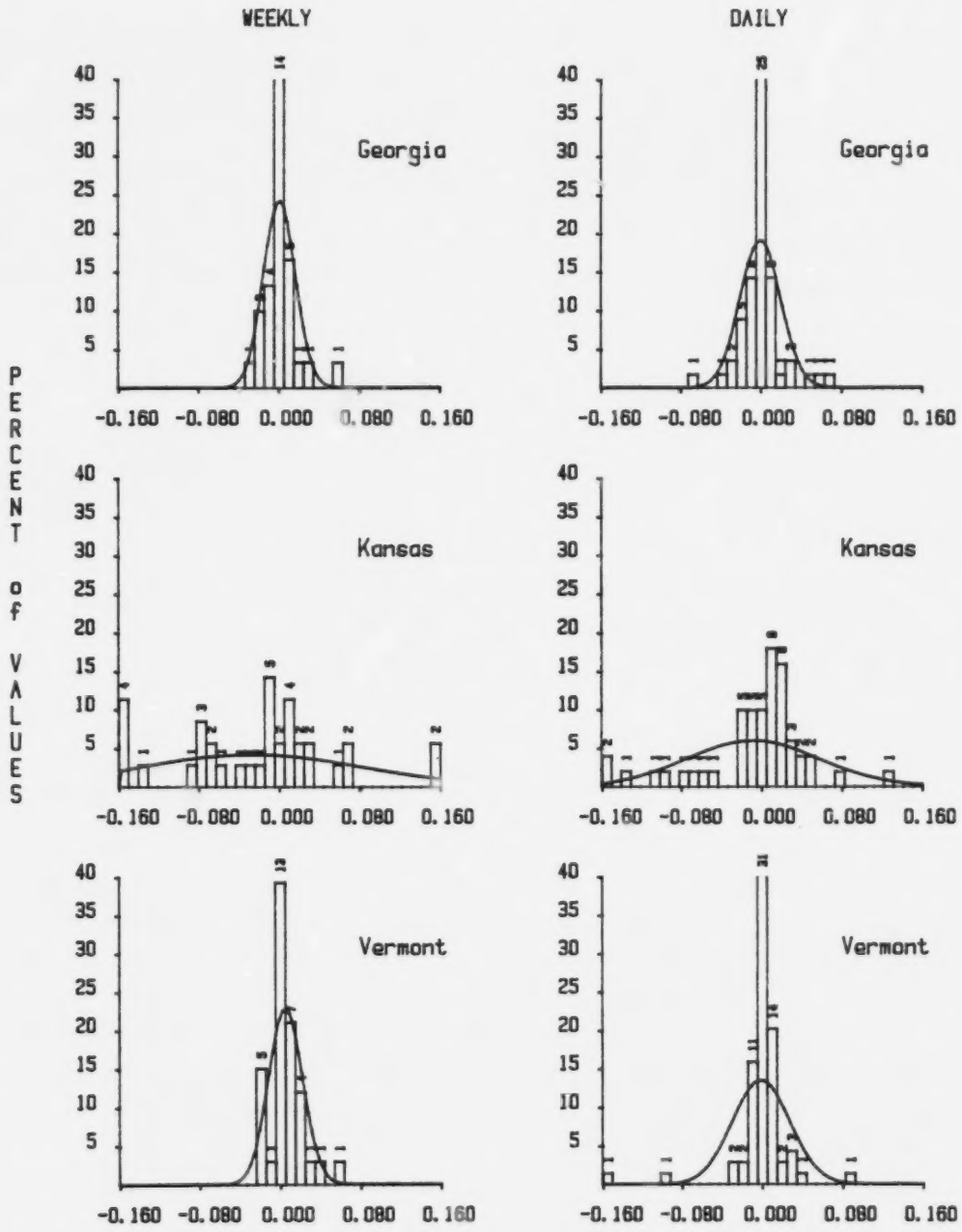

FIGURE 5-7. Distributions of collocated differences for calcium in mg/l. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent the values at the given abscissa and beyond.

Table 5-3

DAILY AND WEEKLY CONCENTRATION SAMPLER BIAS

Analyte	Daily Sampling			Weekly Sampling		
	RD (%)[a]	RSD (%)[b]	N	RD (%)[a]	RSD (%)[b]	N
			Uvalda, GA			
Precipitation	-1.7[W]	3.9	63	-0.0	9.2	34
H^+	-4.1	12.2	57	0.0	17.4	32
$SO_4^=$	-2.4[W]	5.9	57	0.0	13.6	32
NO_3^-	-2.8[W]	5.4	57	-4.5	22.5	32
NH_4^+	-3.3	21.3	57	-2.9	46.3	32
Cl^-	-0.8[W]	13.0	57	1.8	8.3	32
Na^+	-2.8[W]	14.0	57	1.3	17.2	32
K^+	-7.0	58.8	57	-2.8	30.6	32
Ca^{2+}	-2.7	21.7	57	1.5	15.0	32
Mg^{2+}	0.0	18.5	57	-2.3	11.8	32
			Lancaster, KS			
Precipitation	-1.3[W]	5.1	71	0.4[W]	4.1	38
H^+	-6.1	18.2	69	12.5	37.5	36
$SO_4^=$	-2.6	11.7	69	-2.8	9.9	36
NO_3^-	-0.2	21.7	69	-1.2	9.0	36
NH_4^+	-7.6[W]	18.6	69	-3.3	22.2	36
Cl^-	-7.0	44.2	69	-5.0	24.4	36
Na^+	-11.4	41.8	69	-3.0	15.1	36
K^+	-7.0	71.9	69	-20.4	102.0	36
Ca^{2+}	0.3	20.7	69	-7.1	22.9	36
Mg^{2+}	4.3	19.6	69	-14.5	48.2	36

Table 5-3 (Concluded)

Analyte	Daily Sampling RD (%)[a]	Daily Sampling RSD (%)[b]	Daily Sampling N	Weekly Sampling RD (%)[a]	Weekly Sampling RSD (%)[b]	Weekly Sampling N
			Underhill, VT			
Precipitation	-1.5[W]	4.5	132	-3.2[W]	15.3	50
H^+	0.0	7.9	126	-4.1	20.4	48
$SO_4^=$	-0.6	4.7	124	-0.5	7.4	48
NO_3^-	-0.3	5.5	124	-4.2[W]	30.4	48
NH_4^+	-2.7	22.4	121	1.8	16.2	48
Cl^-	-1.8	22.5	124	-4.7	52.1	48
Na^+	-5.8	25.2	117	-2.5	53.2	48
K^+	-4.0	52.0	118	0.0	109.1	48
Ca^{2+}	-2.5	20.2	117	1.8	20.0	48
Mg^{2+}	0.0	21.0	117	0.0	28.6	48

(a) RD = $(\overline{d}/\overline{C})$ x 100, where $\overline{d}$ and $\overline{C}$ are the mean collocated difference and average concentration.

(b) RSD = $(SD/\overline{C})$ x 100, where SD is the standard deviation of the collocated differences.

W = Sampler bias for the collocated pair significantly different from zero based on the Wilcoxon signed-rank test.

less than 4 percent. Bias for a single ion suggests contamination problems, but the nitrate bias at the Vermont site is less than five percent.

Measurement System Precision for Paired Samples

The pooled standard deviations (S_p), the relative standard deviations (RS_p, the S_p divided by mean concentration), the median absolute collocated difference (MACD), and the relative MACD (RACD, the MACD divided by median concentration) are listed in Table 5-4. Most of the RACD values are less than 10 percent except for Na^+ and Ca^{2+} at the Georgia site and K^+ at all three sites. The RS_p values are generally less than 20 percent except for K^+, which is as high as 50 percent at the Georgia site. The large variation in pair differences for K^+ may be due to contamination or adsorption-desorption phenomena from the plastic containers. Dynamic blanks for the collector buckets frequently yielded K^+ concentrations similar to those of the precipitation samples. Similar results were found by Sisterson et al. (2).

The MACD precision estimates for daily concentrations in Table 5-4 are representative of the MACDs for collocated daily samplers in the EPRI-SURE and UAPSP networks (3,4). For example, in the EPRI-SURE and UAPSP networks (1978 to 1981), MACDs for daily H^+ concentrations ranged from 0.0008 to 0.0106 mg/l and $SO_4^=$ MACDs ranged from 0.035 to 0.055 mg/l. The MACDs for the three sites in this study are within those ranges; the same is true for all of the major ions and most of the minor ions. Since the EPRI-SURE and UAPSP networks cover the northeastern United States, precision of the three sites in this study can be considered generally representative of precision of collocated monitors in the Northeast.

As stated in Section 4, the two estimates of precision can be used to compare the number of samples required under daily and weekly sampling to detect a specific trend in time if linear techniques (i.e., t-tests) are used to test for trends. If the daily S_p is the same as the weekly S_p for a particular analyte, then the same number of daily samples as weekly samples would be required to detect the same trend. If the daily S_p is half that of the weekly S_p, then one-quarter as many daily samples as weekly samples would be required to detect the same trend over time. To put it another way, if the daily S_p is half that of the weekly S_p, then a study with daily data would be able to detect a trend of half the magnitude of the smallest trend that could be detected with the same number of weekly samples. Of

Table 5-4

MEASUREMENT SYSTEM PRECISION (mg/l) FOR DAILY AND WEEKLY SAMPLES

Analyte	Daily Sampling				Weekly Sampling			
	S_p[a]	RS_p(%)[b]	MACD[c]	RACD(%)[d]	S_p	RS_p(%)	MACD	RACD(%)
				Uvalda, GA				
Precip (grams)	36.6	3.0	22.0	2.9	178.1	7.3	25.0	1.3
H^+	0.0022	9.0	0.0009	5.1	0.0028	12.1	0.0014	9.1
$SO_4^=$	0.062	4.5	0.039	3.2	0.138	9.5	0.042	3.5
NO_3^-	0.038	4.3	0.028	3.8	0.138	16.0	0.019	2.7
NH_4^+	0.028	15.1	0.012	9.2	0.066	32.3	0.014	9.9
Cl^-	0.035	9.1	0.012	4.2	0.030	5.9	0.007	2.0
Na^+	0.022	10.0	0.009	5.5	0.036	12.0	0.008	3.8
K^+	0.018	41.5	0.005	18.7	0.008	21.4	0.005	16.1
Ca^{2+}	0.017	15.3	0.006	8.2	0.014	10.8	0.007	7.3
Mg^{2+}	0.0035	10.6	0.002	8.1	0.0036	8.4	0.0015	5.1

Table 5-4 (Continued)

Analyte	Daily Sampling				Weekly Sampling			
	S_p[a]	RS_p(%)[b]	MACD[c]	RACD(%)[d]	S_p	RS_p(%)	MACD	RACD(%)
				Lancaster, KS				
Precip (grams)	28.7	3.7	17.3	3.0	46.0	2.9	18.1	1.7
H^+	0.0036	21.7	0.0010	8.2	0.0044	27.6	0.0014	12.5
$SO_4^=$	0.170	8.4	0.062	3.5	0.132	7.2	0.083	4.7
NO_3^-	0.250	15.3	0.057	4.3	0.102	6.4	0.061	4.3
NH_4^+	0.082	14.1	0.031	7.6	0.075	15.7	0.031	7.2
Cl^-	0.045	31.4	0.010	9.4	0.021	17.4	0.010	9.2
Na^+	0.024	30.4	0.005	9.5	0.007	10.8	0.005	8.5
K^+	0.029	50.7	0.005	14.6	0.036	72.6	0.005	14.9
Ca^{2+}	0.082	14.5	0.021	6.8	0.082	16.7	0.057	15.5
Mg^{2+}	0.0065	14.1	0.0022	6.6	0.0146	35.1	0.0038	11.8

Table 5-4 (Concluded)

Analyte	Daily Sampling				Weekly Sampling			
	S_p[a]	RS_p(%)[b]	MACD[c]	RACD(%)[d]	S_p	RS_p(%)	MACD	RACD(%)
				Underhill, VT				
Precip (grams)	20.7	3.3	10.3	3.1	164.1	10.9	27.0	2.3
H^+	0.0028	5.6	0.0017	4.0	0.0071	14.6	0.0021	4.3
$SO_4^=$	0.070	3.3	0.037	2.7	0.105	5.2	0.059	3.8
NO_3^-	0.068	3.9	0.042	2.9	0.380	21.5	0.044	3.0
NH_4^+	0.048	15.9	0.008	3.9	0.032	11.4	0.011	5.2
Cl^-	0.018	15.9	0.005	7.6	0.039	36.6	0.004	6.6
Na^+	0.009	18.2	0.003	14.1	0.015	37.2	0.003	12.2
K^+	0.009	36.7	0.003	21.8	0.017	76.3	0.003	21.4
Ca^{2+}	0.017	14.3	0.006	12.5	0.016	14.0	0.008	13.1
Mg^{2+}	0.0028	14.8	0.0009	10.0	0.0035	20.0	0.0012	13.2

(a) $S_p = \left(\sum_{i=1}^{N} d_i^2/2N \right)^{1/2}$, where d_i is the collocated pair difference for the ith species and N is the number of collocation events.

(b) $RS_p(\%) = (S_p/\overline{C}) \times 100$, where $\overline{C}$ is the average concentration.

(c) MACD = median of absolute collocated pair differences.

(d) RACD (%) = (MACD/median concentration) x 100.

course, in a given time period there are more daily samples than weekly samples, so this must be taken into account. In the three sites in this study, there are two to three times as many daily samples as weekly samples; i.e., precipitation events occurred two to three times per week at the sites. So if the pooled standard deviation of the daily data is the same as that of the weekly data, but there are twice as many daily events as weekly events in a study, then a trend in time of a specified magnitude will be detected in daily samples in approximately one-quarter the time it would take to detect a trend from weekly samples.

The relative efficiency of the two sampling protocols to detect a trend of a certain magnitude with a specified probability is thus estimated by the ratio of the weekly and daily pooled standard deviations, or alternatively, by the ratio of the weekly and daily median absolute collocated differences. These ratios are shown in Figures 5-8 and 5-9, respectively, for each parameter at each site. The figures show that the majority of the weekly to daily scale ratios are greater than one, i.e., that the daily samples are more precise than weekly samples. The two figures, however, do not always tell the same story. In the case of NO_3^- at the Georgia site, for example, the ratio of the weekly to the daily pooled standard deviation is 3.63, but the ratio of the weekly to the daily MACD is 0.679. This suggests that differences in precision between daily and weekly measurements may have more to do with exactly how precision is defined than with any practically significant difference between the two methods.

Both the ratio of weekly to daily samples and the number of precipitation events per week (or number of daily samples per week) must be considered to determine how much more quickly a trend can be detected with daily samples than with weekly samples. These calculations are listed in the table below for the ratio of weekly to daily precision values that are typical in this study.

Ratio of Weekly-to-Daily Precision	Number of Daily Samples Per Week				
	1.0	1.5	2.0	2.5	3.0
1.0	1.00	0.44	0.25	0.16	0.11
1.2	0.69	0.31	0.17	0.11	0.08
1.4	0.51	0.23	0.13	0.08	0.06
1.6	0.39	0.17	0.10	0.06	0.04

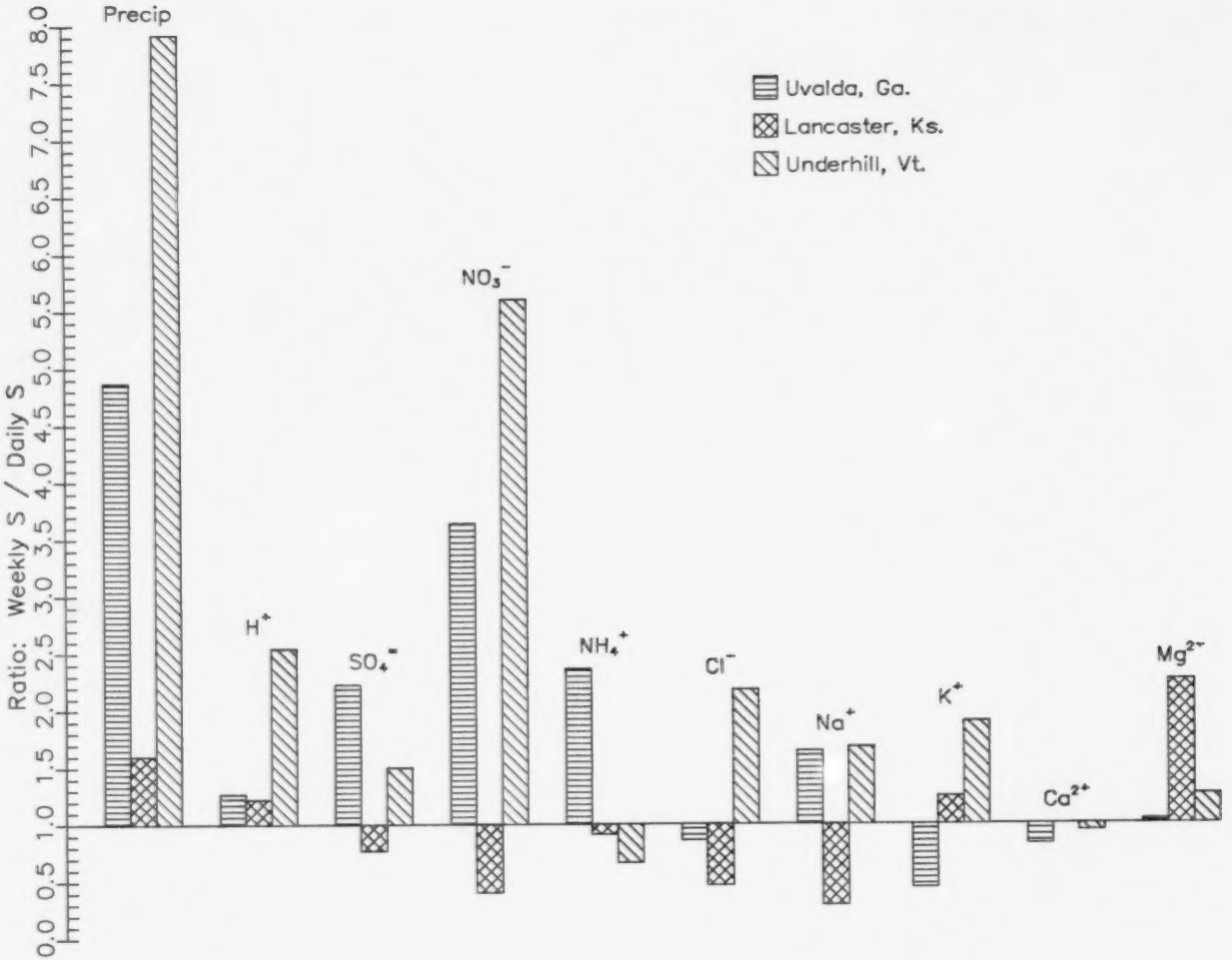

Figure 5-8. Ratios of Weekly to Daily Pooled Standard Deviation from Collocated Samplers.

Figure 5-9. Ratios of Weekly to Daily Median Absolute Collocated Difference.

Thus we see, for example, that if there are two daily samples per week and weekly sampling is 40 percent less precise than daily sampling (ratio = 1.4), then a trend of a specified magnitude can be detected from daily samples in only 13 percent of the time it would take to detect the same trend from weekly samples. A ratio of weekly-to-daily precision of 1.4 is about the average across the three sites for H^+ and $SO_4^=$, the two most important ions. Although the daily samples will reveal trends at a much faster rate, cost must be considered as a factor. Since daily sampling is considerably more expensive than weekly sampling, the costs may outweigh the benefits of daily sampling.

The number of monitors in a geographical area is another factor to consider when designing a network. One may be able to more easily detect trends in an area with more weekly monitors than with a smaller set of daily samplers. This study was not designed to determine how the number of monitors in an area affects trend estimation.

DERIVED VERSUS MEASURED WEEKLY CONCENTRATIONS

The median and mean daily, weekly, and derived weekly concentrations for each site are summarized in Table 5-5. In all cases the mean values are larger than the median values, indicating that the ion concentration distributions are skewed, with long positive tails. The Vermont site has the highest mean H^+, $SO_4^=$, and NO_3^- concentrations. Kansas has the lowest H^+, the highest NH_4^+, and, except for Na^+, the greatest metal ion concentrations. The Georgia site has the lowest concentrations of acid anions and ammonium, but the highest Na^+ concentrations. The median, mean, and standard error of the mean of the site concentrations for both measured weekly and derived weekly samples for rain, snow, and mixed samples are given in Appendix B (Tables B-1, B-2 and B-3, respectively).

Method Bias By Site and Type of Precipitation

Method difference is defined as the derived weekly minus the measured weekly value. Figures 5-10 through 5-12 contain histograms of the differences between derived weekly and measured weekly concentrations of the major ions and precipitation at each of the three sites. The curves in the figures represent the Gaussian distribution with the same mean and standard deviation as the displayed

Table 5-5

SUMMARY OF MEDIAN AND MEAN SITE CONCENTRATIONS (mg/l)

Analyte	Daily Measured		Weekly Measured		Derived Weekly	
	Median	Mean	Median	Mean	Median	Mean
Precip (grams)						
Georgia	759.	1285.	1832.	2312.	1848.	2362.
Kansas	573.	785.	1025.	1544.	891.	1498.
Vermont	329.	620.	1179.	1538.	1170.	1561.
H^+						
Georgia	0.019	0.025	0.015	0.022	0.013	0.022
Kansas	0.011	0.016	0.014	0.016	0.016	0.017
Vermont	0.040	0.058	0.045	0.047	0.048	0.050
$SO_4^=$						
Georgia	1.212	1.494	1.132	1.329	0.951	1.261
Kansas	1.745	2.056	1.690	1.781	1.477	1.729
Vermont	1.386	2.363	1.521	1.990	1.543	2.014
NO_3^-						
Georgia	0.726	0.948	0.628	0.802	0.627	0.772
Kansas	1.386	1.704	1.405	1.591	1.362	1.543
Vermont	1.466	2.056	1.271	1.755	1.285	1.818
NH_4^+						
Georgia	0.132	0.201	0.117	0.175	0.125	0.175
Kansas	0.398	0.596	0.425	0.469	0.387	0.472
Vermont	0.215	0.334	0.205	0.157	0.157	0.278

Table 5-5 (Concluded)

Analyte	Daily Measured		Weekly Measured		Derived Weekly	
	Median	Mean	Median	Mean	Median	Mean
Cl^-						
Georgia	0.284	0.452	0.304	0.415	0.302	0.400
Kansas	0.125	0.151	0.100	0.114	0.110	0.120
Vermont	0.071	0.120	0.065	0.106	0.068	0.110
Na^+						
Georgia	0.160	0.260	0.210	0.240	0.160	0.220
Kansas	0.055	0.088	0.051	0.057	0.054	0.060
Vermont	0.021	0.052	0.024	0.040	0.022	0.040
K^+						
Georgia	0.029	0.049	0.029	0.031	0.030	0.034
Kansas	0.036	0.060	0.035	0.048	0.035	0.044
Vermont	0.013	0.041	0.014	0.021	0.010	0.016
Ca^{2+}						
Georgia	0.077	0.120	0.088	0.114	0.065	0.093
Kansas	0.317	0.597	0.342	0.465	0.403	0.460
Vermont	0.047	0.129	0.057	0.111	0.049	0.098
Mg^{2+}						
Georgia	0.025	0.039	0.029	0.035	0.026	0.032
Kansas	0.035	0.049	0.032	0.039	0.030	0.037
Vermont	0.009	0.022	0.008	0.018	0.007	0.015

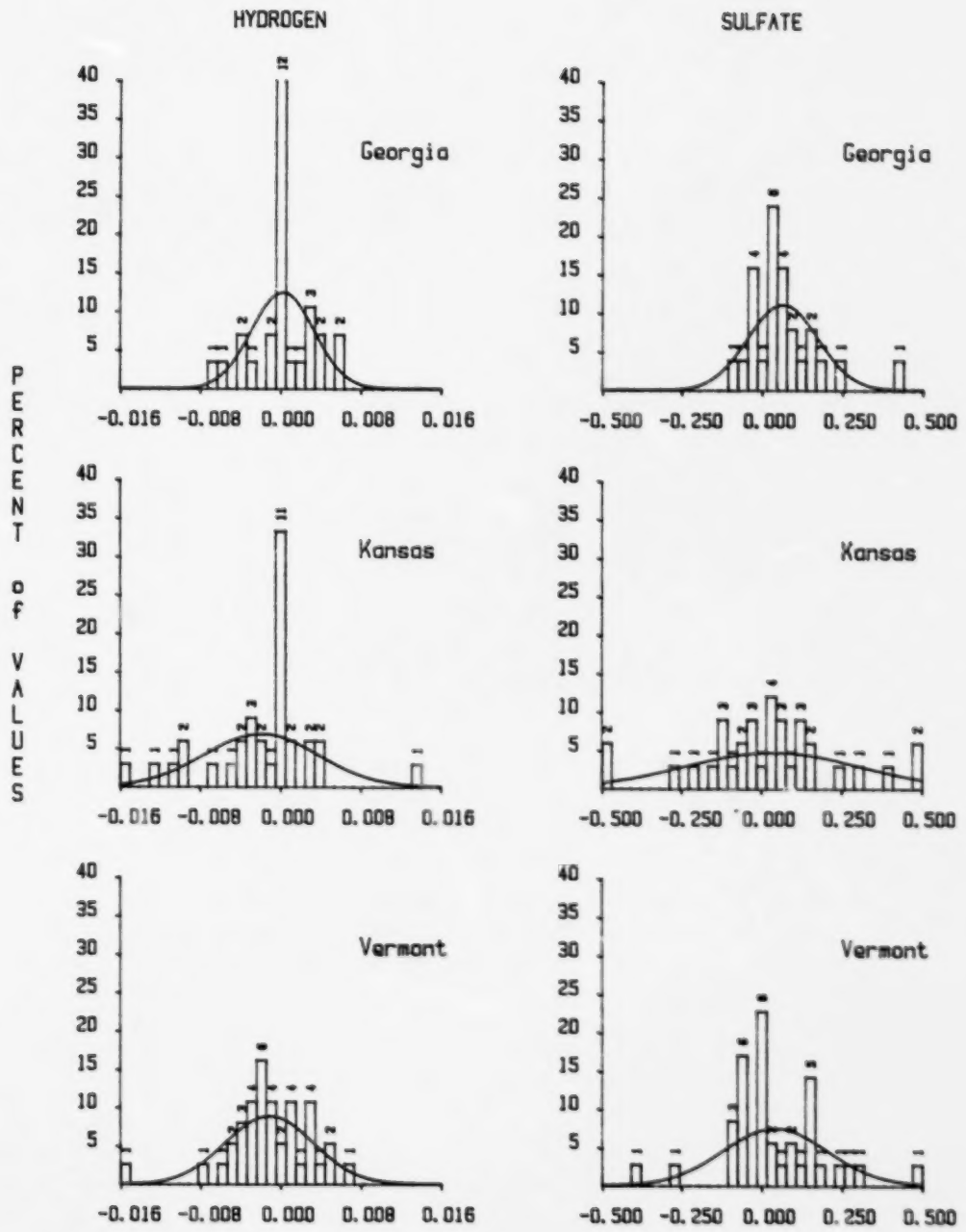

FIGURE 5-10. Derived weekly-measured weekly data for hydrogen and sulfate ions in mg/l. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent values at the given abscissa and beyond.

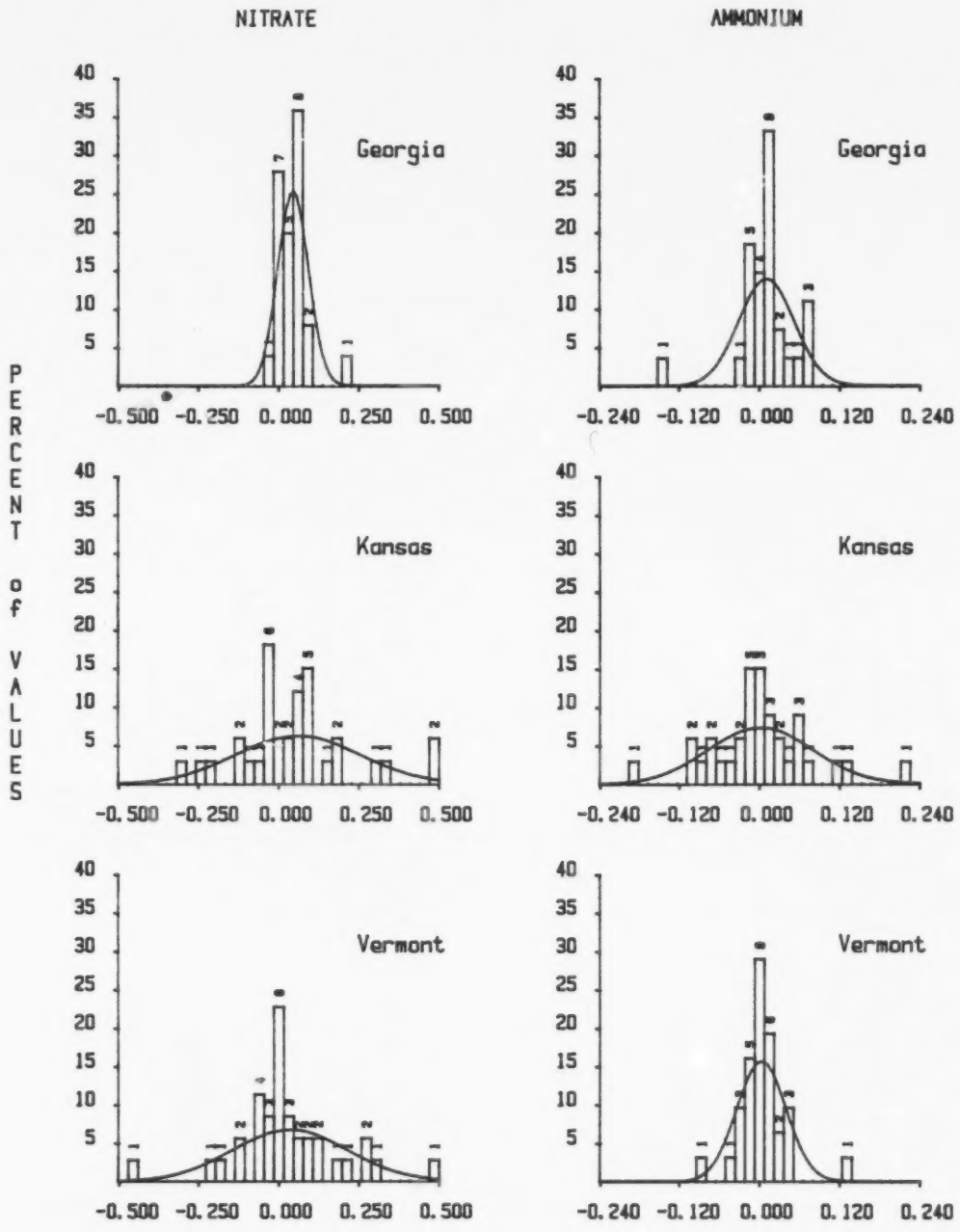

FIGURE 5-11. Derived weekly-measured weekly data for nitrate and ammonium ions in mg/l. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent values at the given abscissa and beyond.

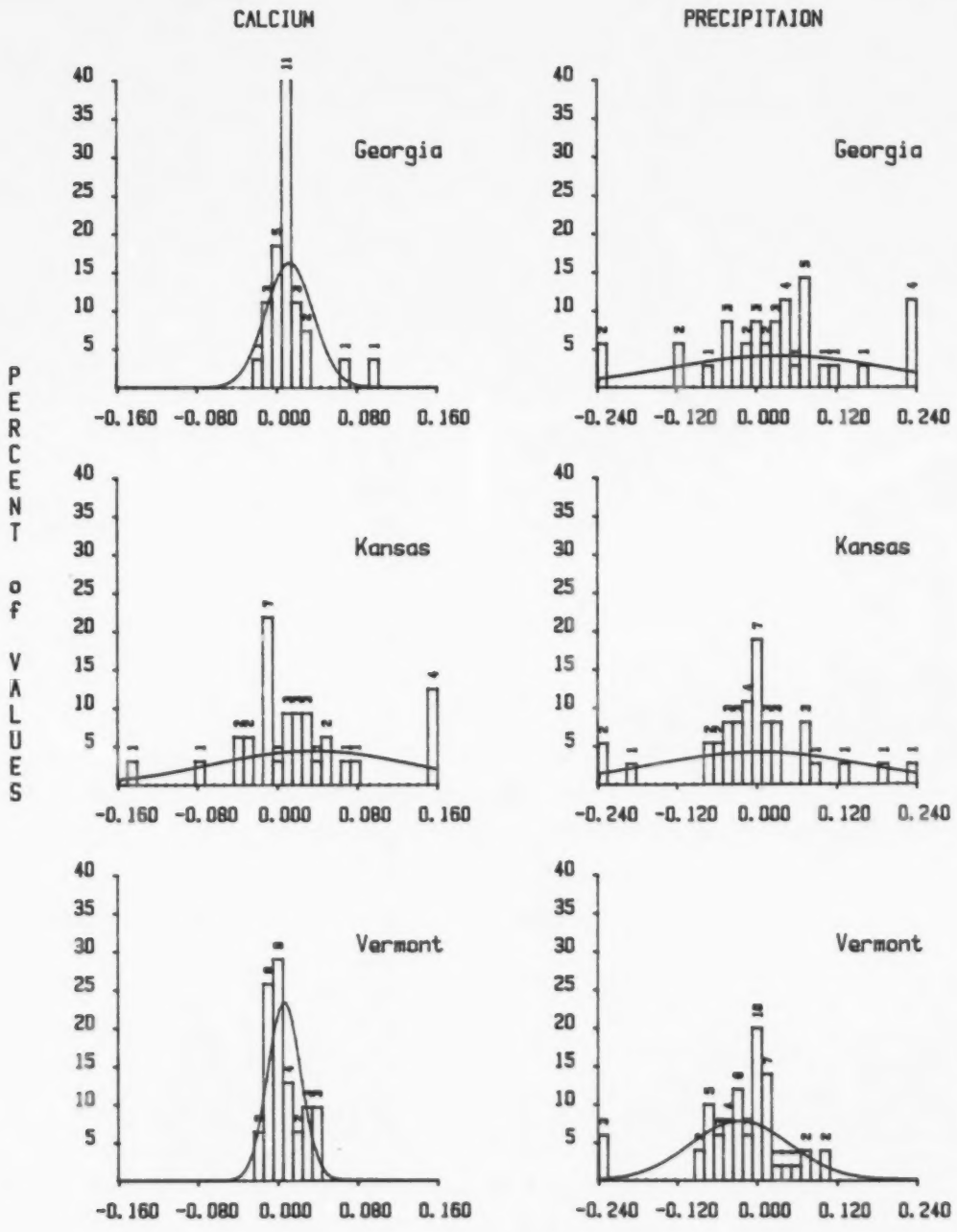

FIGURE 5-12. Derived weekly-measured weekly data for calcium ion in mg/l and predipitation mass in kg. The curve represents the Gaussian distribution with the same mean and standard deviation as the displayed data. The extreme bars represent values at the given abscissa and beyond.

data. The collocated sampler differences (Figures 5-2 through 5-7), appear to be symmetric with more values clustered about the center and longer tails than Gaussian distributions. The median or the mean method difference may be called the method bias. Relative differences between derived weekly and measured weekly concentrations for the four major ions are shown in Figures 5-13 and 5-14. Most of the relative differences are within plus or minus 20 percent. From a comparison of these plots with those in Appendix C, it appears that the larger relative differences occur at low depositions.

The median or mean method difference may be called the method bias. These means and medians and relative bias (mean bias divided by mean derived weekly concentration) for all the precipitation types combined are listed for the three sites in Table 5-6. Statistically significant biases according to the Wilcoxon test are noted in the table, and Figure 5-15 provides a graphical summary of the relative bias for each analyte at each site. The biases are statistically significant for most ions at the Georgia site. All of the significantly different concentrations are higher for the weekly samplers. Possibly the ion concentration is increased by some evaporation of precipitation from the weekly collectors or the warmer Georgia climate causes weekly samples to be more unstable. On the other hand, the weekly samplers in Georgia actually collected slightly more precipitation, so the differences may be attributable also to differences in collection efficiency. But this factor would be independent of the sample collection time, and would reflect a possibility of catching more of the initial rainfall which is often more concentrated in constitutents.

At the Kansas site the biases are both positive and negative. Although some of the relative biases are large, none is statistically significant because of the large measurement variability associated with these ions. For hydrogen ion the mean concentration, 0.016 mg/l, for the Kansas site (Table 5-5) is the smallest of the three sites. In general, the lower the hydrogen ion concentration the lower is the specific conductance of the solution. Low conductivity increases the difficulty to make accurate pH measurements and yields poor precision (Table 5-4). For potassium, the other ion of large bias, many of the concentrations are near the analytical detection level which also results in poor precision for the measurement. At the Vermont site, the daily samplers contained slightly more precipitation than the weekly samplers (Table 5-2); the difference is statistically though not practically signficant. There are statistically significant negative biases only in the concentrations of potassium, calcium, and magnesium ion.

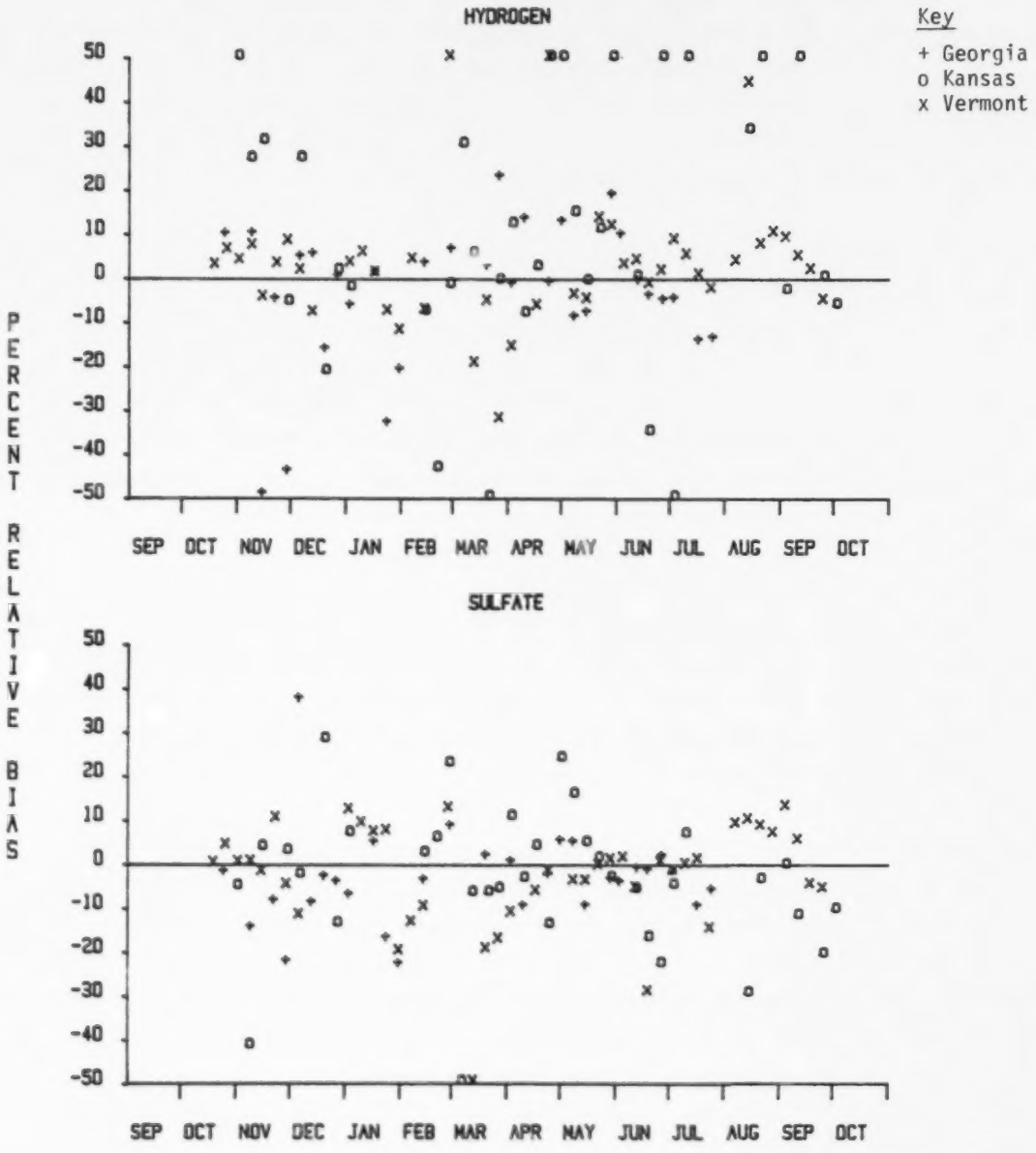

FIGURE 5-13. Weekly percent relative method bias for hydrogen and sulfate. Differences beyond 50 percent are truncated.

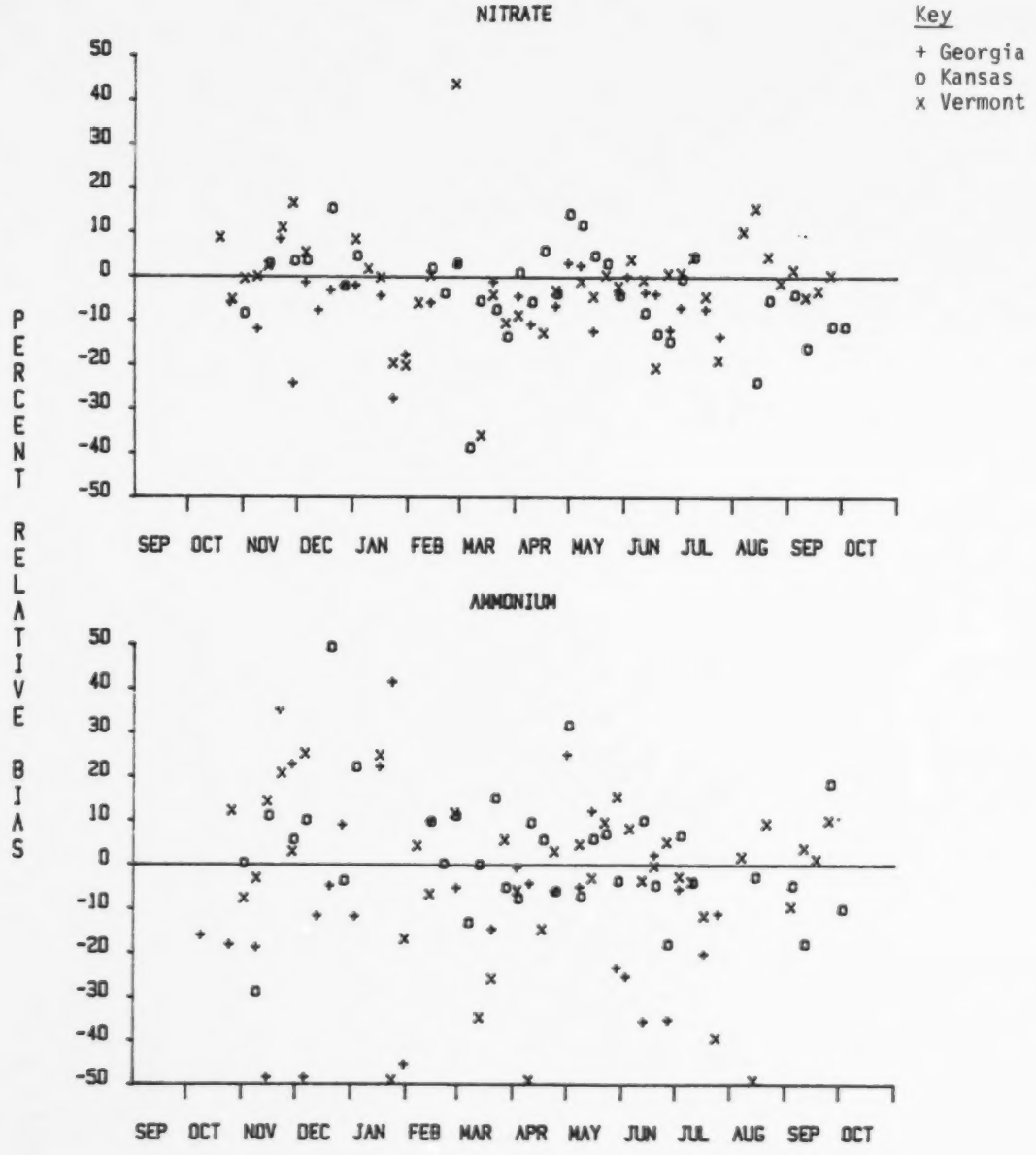

FIGURE 5-14. Weekly percent relative method bias for nitrate and ammonium. Differences beyond 50 percent are truncated.

Table 5-6

METHOD BIAS (DERIVED WEEKLY - MEASURED WEEKLY) CONCENTRATION (mg/l) FOR ALL SAMPLES

	Georgia			Kansas			Vermont		
Analyte	Median Bias	Mean Bias	Relative Bias (%)[a]	Median Bias	Mean Bias	Relative Bias (%)[a]	Median Bias	Mean Bias	Relative Bias (%)[a]
Precip(grams)	-34.6	-19.2	-0.8	0.2	-37.4	-2.5	17.4[W]	22.2	1.4
H^+	-0.0003	-0.0004	-1.7	0.0007	0.0027	16.0	0.0022	0.0014	2.7
$SO_4^=$	-0.037[W]	-0.053	-4.2	-0.041	-0.030	-1.7	0.002	-0.036	-1.8
NO_3^-	-0.043[W]	-0.055	-7.1	-0.020	-0.044	-2.9	0.006	0.006	0.3
NH_4^+	-0.011[W]	-0.008	-4.5	0.0056	-0.0004	-0.1	0.004	-0.007	-2.4
Cl^-	-0.009[W]	-0.014	-3.5	0.003	0.002	1.6	0.003	-0.001	-0.7
Na^+	-0.001[W]	-0.018	-8.1	0.0003	-0.0003	-0.5	0.001	-0.001	-3.0
K^+	-0.000	0.002	7.2	-0.001	-0.009	-20.4	-0.002[W]	-0.005	-33.8
Ca^{2+}	-0.006[W]	-0.011	-11.5	-0.009	-0.048	-10.3	-0.006[W]	-0.008	-7.8
Mg^{2+}	-0.0008	-0.0016	-5.1	-0.0014	-0.0045	-12.1	-0.0009[W]	-0.0016	-10.6

W = Significant differences for weekly vs. derived concentrations, based on Wilcoxon signed-ranks test.

(a) Relative bias = mean bias/mean derived weekly concentration.

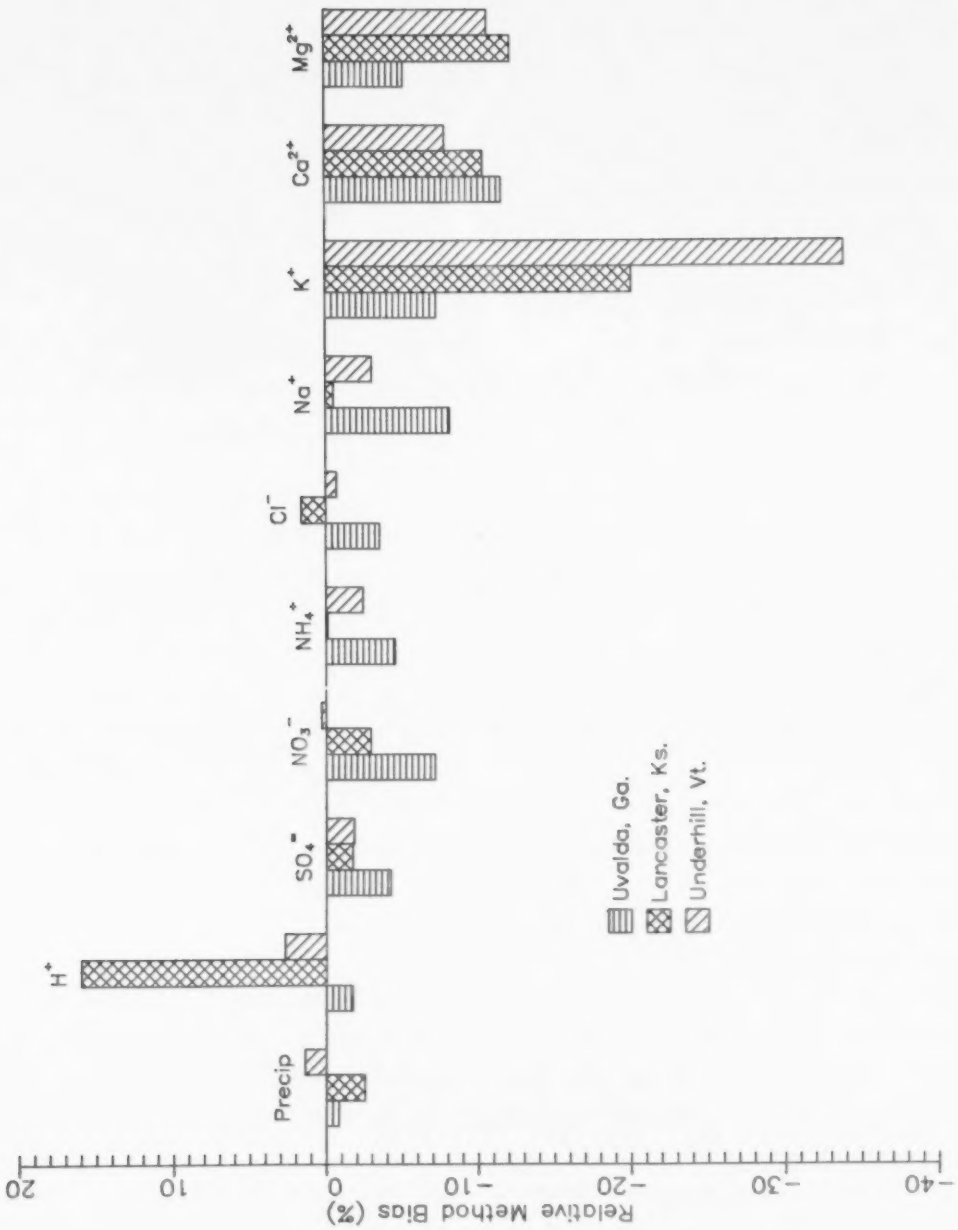

Figure 5-15. Percent Relative Method Bias (100 * means bias/mean derived weekly concentration).

The percent biases in Figure 5-15 are predominantly negative; i.e., the concentrations are higher in the weekly samplers. The only case in which concentrations are much larger in the daily samples is for H^+ at the Kansas site (16 percent). The largest relative biases are observed for K^+, especially at the Kansas site (-20.4%) and Vermont site (-33.8%). At all three sites concentrations of Ca^{2+} and Mg^{2+} are also relatively large in the weekly samplers, typically about 10 percent larger, which might be attributable to contamination of weekly samples by re-suspended soil particles. Relative precipitation bias is practically insignificant at all three sites, no larger than 2.5 percent. However, small rainfall events (less than 0.51 mm) are not included in the derived weekly precipitation amounts but they are included in the measured weekly precipitation amounts, so there is actually a smaller bias in precipitation amount than is indicated in Table 5-6. Evaporation alone cannot explain the observed method bias. Other feasible explanations are contamination during the seven-day storage, potential contribution of highly concentrated trace samples (which are included in the weekly samples but not in the daily composites), and instability of weekly samples.

Table 5-7 compares the mean and relative mean bias for rain samples separately and all precipitation types combined. The Georgia site has relative bias values under 10 percent for all the observables except Ca^{2+} for which the bias is 11.5 percent. For Kansas, the relative bias for rain sample values is 6.0 percent or less, except for H+, for which it is 18 percent. If all the precipitation types are considered, results similar to those for rain are obtained, except for Cl^-, K^+, Ca^{2+}, and Mg^{2+}; for Cl^-, the relative bias is now smaller, whereas for the cations it is larger. For Vermont, the relative bias values for rain samples and all precipitation types combined are similar, and except for K^+, are less than 11 percent. One-way ANOVAs with the Welch test indicate that for rain samples there are significant differences in the mean bias among the sites for Na^+ only, whereas when all precipitation types are combined, significant differences among the sites occur both for Na^+ and for H^+. These results indicate that there is little difference among the sites in the bias for any of the observables except for Na^+ for rain samples and for Na^+ and H^+ for all precipitation types. In addition, except for K^+, the differences between weekly and daily composite samples are generally under 12 percent, and for the major ions (H^+, NH_4^+, $SO_4^=$, and NO_3^-) they are typically much less (H^+ for Kansas is the exception). These results indicate that errors in annual average concentrations due to method bias are likely to be

Table 5-7

COMPARISON OF SITE MEAN AND RELATIVE CONCENTRATION BIAS (mg/l) FOR RAIN AND ALL SAMPLES

Analyte		Georgia[a]		Kansas		Vermont		Sig. Diff. Among Sites[c]
		Mean Bias	Relative Bias (%)[b]	Mean Bias	Relative Bias (%)	Mean Bias	Relative Bias (%)	
Precip(grams)	Rain	-19.2	-0.8	-20.7	-1.2	2.3	0.1	No
	All			-37.4	-2.5	22.2	1.4	No
H^+	Rain	-0.0004	-1.7	0.0024	18.0	0.0019	3.4	No
	All			0.0027	16.0	0.0010	2.7	Yes
$SO_4^=$	Rain	-0.053	-4.2	0.038	2.2	-0.056	-2.0	No
	All			-0.030	-1.7	-0.036	-1.8	No
NO_3^-	Rain	-0.055	-7.1	-0.022	-1.6	-0.024	-1.6	No
	All			-0.044	-2.9	0.006	0.3	No
NH_4^+	Rain	-0.008	-4.5	-0.0001	-0.02	-0.008	-2.1	No
	All			-0.0004	-0.1	-0.007	-2.4	No
Cl^-	Rain	-0.014	-3.5	0.007	6.0	0.001	0.9	No
	All			0.002	1.6	-0.001	-0.7	No
Na^+	Rain	-0.018	-8.1	0.001	1.6	0.003	6.4	Yes
	All			-0.0003	-0.5	-0.001	-3.0	Yes

Table 5-7 (Concluded)

Analyte		Georgia[a] Mean Bias	Georgia[a] Relative Bias (%)[b]	Kansas Mean Bias	Kansas Relative Bias (%)	Vermont Mean Bias	Vermont Relative Bias (%)	Sig. Diff. Among Sites[c]
K^+	Rain	-0.002	-7.2	-0.001	-2.5	-0.006	-31.6	No
	All			-0.009	-20.4	-0.005	-33.8	No
Ca^{+2}	Rain	-0.011	-11.5	-0.028	-5.5	-0.007	-5.4	No
	All			-0.048	-10.3	-0.008	-7.8	No
Mg^{+2}	Rain	-0.002	-5.1	-0.002	-5.0	-0.002	-9.5	No
	All			-0.005	-12.1	-0.002	-10.6	No

(a) All samples collected in Georgia were rain only.

(b) Relative bias (%) = 100 x mean bias/mean derived weekly concentration.

(c) Significant differences in the mean bias are detected by the Welch test, which does not assume equal variances for the ANOVA.

small, and therefore do not seem to have much practical significance. Furthermore, since method bias is more or less constant from site to site, conclusions about the geographic pattern of concentrations are not likely to be affected by the choice of method if these sites are representative.

Method Bias By Season

Although there is obviously some confounding of the effects of precipitation type, site (there is no snow in Georgia), and season the effect of season on the concentration bias was also examined for the three sites individually and for all sites combined. For the fall quarter, the 1983 and 1984 data were combined. The biases for the weekly derived minus weekly measured concentrations together with the respective Wilcoxon test results are presented in Table 5-8 for all precipitation types and all sites combined. Significant bias is seen for nitrate and calcium in the spring but for no analytes in the summer or winter quarters. However, there is significant bias for H^+, $SO_4^=$, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} in the fall. The measured weekly concentrations are larger than the derived ones in all cases of significant bias except for H^+ in the fall quarter. Higher Ca^{2+} and Mg^{2+}, which generally come from basic soil dust, are expected to yield lower H^+ in the weekly samples. Even if the Na^+ and H^+ results are confounded by site effects, the results still indicate that a majority of the analytes show significant bias in the fall. The significant fall season biases are difficult to explain. It is expected that the largest number of freeze-thaw cycles would occur in the fall and that may affect some gas and ion solubilities.

In Table 5-9 the bias and relative bias for rain and for all precipitation samples are summarized by season for all sites combined. In accord with the results in Table 5-8, the largest relative bias for all the observables except potassium in rain occurs in the fall. For the four major ions, the relative biases are under 7 percent in rain samples and 13 percent in all samples. ANOVA tests show that there are no significant differences in bias due to season for all observables except Na^+ and Mg^{2+} in rain samples and Cl^- in all precipitation samples. Thus the concentration bias between weekly and daily samples is similar across seasons for most of the constituents.

Table 5-8

DERIVED WEEKLY - MEASURED WEEKLY CONCENTRATION BIAS (mg/l) BY SEASON

Analyte	Winter		Spring		Summer		Fall[a]	
	Median Bias	Mean Bias	Median Bias	Mean Bias	Median Bias	Mean Bias	Median Bias	Mean Bias
Precip(grams)	-4.8	-14.7	-1.5	-11.0	10.3	4.1	10.4	25.2
H^+	0.0000	-0.0011	0.0003	0.0000	0.0004	-0.0019	0.0021[W]	0.0014
$SO_4^=$	-0.022	-0.000	-0.023	-0.116	-0.035	-0.059	-0.036[W]	0.022
NO_3^-	-0.003	0.050	-0.041[W]	-0.072	-0.021	-0.074	-0.027	-0.124
NH_4^+	0.006	0.010	-0.010	-0.004	-0.011	-0.035	-0.004	-0.040
Cl^-	0.004	0.005	-0.003	-0.004	-0.002	-0.003	-0.010[W]	-0.037
Na^+	0.000	-0.004	0.000	-0.006	0.001	-0.001	-0.002[W]	-0.023
K^+	-0.002	-0.003	-0.001	0.000	0.001	0.072	-0.005[W]	-0.028
Ca^{2+}	-0.003	-0.006	-0.009[W]	-0.021	-0.003	0.068	-0.013[W]	-0.066
Mg^{2+}	-0.0003	-0.0007	-0.001	-0.002	-0.001	0.013	-0.003[W]	-0.008

(a) The fall data combine 1983 and 1984 fall measurements.

W = Significant median bias based on Wilcoxon signed-ranks test.

Table 5-9

COMPARISON OF MEAN AND RELATIVE CONCENTRATION BIAS (mg/l) FOR RAIN AND ALL SAMPLES BY SEASON

Observable		Winter		Spring		Summer[a]		Fall[b]		Sig. Diff. Among Seasons (0.05)[d]
		Mean Bias	Relative Bias(%)[c]	Mean Bias	Relative Bias(%)	Mean Bias	Relative Bias(%)	Mean Bias	Relative Bias(%)	
Precip(grams)	Rain	-79.8	-3.5	-5.1	-0.2	4.1	2.0	-22.4	-1.5	No
	All	-14.7	-0.9	-11.0	-0.5			25.2	1.3	No
H^+	Rain	-0.0010	-4.3	-0.0002	-1.3	-0.0019	-3.7	0.0008	1.7	No
	All	-0.0011	-3.1	0.0000	0.4			0.0014	3.6	No
$SO_4^=$	Rain	0.006	0.6	-0.046	-3.1	-0.059	-1.9	-0.112	-5.7	No
	All	0.000	0.0	-0.116	-7.0			0.022	1.0	No
NO_3^-	Rain	-0.008	-1.2	-0.024	-2.5	-0.074	-3.8	-0.075	-6.5	No
	All	0.050	-2.5	-0.072	6.7			-0.124	-9.0	No
NH_4^+	Rain	0.001	0.1	0.365	3.3	-0.035	-7.0	-0.012	-3.8	No
	All	0.010	4.4	-0.010	-1.0			-0.040	-12.4	No
Cl^-	Rain	0.018	4.7	0.001	0.4	-0.003	-1.1	-0.034	14.5	No
	All	0.005	2.1	-0.004	-2.3			-0.037	-17.3	Yes
Na^+	Rain	0.001	0.5	-0.006	-4.6	-0.001	-1.2	-0.022	-16.9	Yes
	All	-0.004	-3.3	-0.006	-5.9			-0.023	-19.6	No

Table 5-9 (Concluded)

Observable		Winter		Spring		Summer[a]		Fall[b]		Sig. Diff. Among Seasons (0.05)[d]
		Mean Bias	Relative Bias(%)[c]	Mean Bias	Relative Bias(%)	Mean Bias	Relative Bias(%)	Mean Bias	Relative Bias(%)	
K^+	Rain	0.002	11.1	0.001	2.3	0.072	62.2	-0.005	-22.7	No
	All	-0.003	-12.4	0.000	-1.5			-0.028	-119.0	No
Ca^{+2}	Rain	-0.003	-5.1	-0.009	-3.4	0.068	16.0	-0.045	-19.3	No
	All	-0.006	-3.7	-0.021	-8.5			-0.066	-38.4	No
Mg^{+2}	Rain	0.0003	1.1	-0.002	-5.9	0.013	21.7	-0.006	-17.6	Yes
	All	-0.0007	-2.8	-0.002	-8.3			-0.008	-31.2	No

(a) All samples collected in the summer were rain only.

(b) The fall data combine 1983 and 1984 fall measurements.

(c) Relative bias (%) = 100 x mean bias/mean derived weekly concentration.

(d) Significant differences in the mean bias are detected by the Welch test, which does not assume equal variances for the ANOVA.

COMPARISON OF DAILY AND WEEKLY DEPOSITION

Deposition is the mass of a constituent deposited per unit area, and it is of prime importance in the study of effects on the environment. It is not a measured quantity, but the product of two measurements, the analyte concentration and the precipitation depth. Thus errors in deposition values arise from errors in both measurements. The deposition results discussed next consist of precision data and an evaluation of annual and seasonal values from both daily and weekly concentration measurements. The precision of the weighing bucket rain gauge was also calculated to help analyze the deposition results.

Rain Gauge Precision

Collocated rain gauges were installed at the Kansas and Vermont stations. These sites were chosen to test the rain gauge response to the three different precipitation types. Only daily data were evaluated since weekly precipitation depths were obtained by summing the daily values. Summary statistics for rain gauge bias and precision are presented in Tables 5-10 and 5-11, respectively. At both sites, snow samples show the greatest bias, relative bias (10 to 15 percent), and RSD (11 to 15 percent), as expected. Snow capture losses occur from wind effects, as with the samplers, and these losses are not the same for each gauge. On the basis of one-way ANOVA, the Kansas site shows no significant differences among the three precipitation types for either bias or standard deviation, while the Vermont site has significantly different paired differences among the different precipitation types. The bias in the precipitation depth measurements for the collocated gauges at the Vermont site is significant for all precipitation types combined but not for any specific precipitation type. These results indicate that there was a problem with at least one of the gauges at the Vermont site.

The effect of season on rain gauge measurements for both sites is shown in Table 5-12. Comparisons based on separate variance t-tests were made between the two sites for each season, and between seasonal pairs for each site. Results of these comparisons showed a significant difference between the distributions of the two sites for winter only. No significant seasonal differences were detected for the Kansas site. Significant seasonal differences in amount of precipitation

Table 5-10

RAIN GAUGE BIAS (cm) BY PRECIPITATION TYPE
CALCULATED FROM DAILY MEASUREMENTS

Precipitation Type	N	Bias[a]	RD (%)[b]	SD[c]	RSD (%)[d]
		Lancaster, KS			
Rain	70	0.0109	0.9	0.1363	11.0
Snow	4	0.0381	10.5	0.0/90	21.8
Mixed	14	0.0145	1.3	0.0667	6.4
All	88	0.0127	1.1	0.1251	10.7
		Underhill, VT			
Rain	87	-0.0321	-3.1	0.1015	9.8
Snow	30	-0.0694	-14.5	0.0763	15.9
Mixed	24	-0.0096	-1.0	0.0937	8.7
All	141	-0.0362[W]	-3.9	0.0966	10.5

(a) Bias = $\bar{d}$, mean collocated difference.

(b) RD = relative difference, $\bar{d}/\bar{R}$, where $\bar{R}$ is the average rain gauge depth.

(c) SD = standard deviation of the differences.

(d) RSD = relative standard deviation, $SD/\bar{R}$.

W = Bias significantly different from zero based on the Wilcoxon signed-rank test.

Table 5-11

RAIN GAUGE PRECISION (cm) BY PRECIPITATION TYPE
FOR DAILY SAMPLES

Precipitation Type	S_p[a]	RS_p (%)[b]	MACD[c]	RACD (%)[d]
		Lancaster, KS		
Rain	0.0960	7.8	0.0000	0.0
Snow	0.0554	15.3	0.0254	7.1
Mixed	0.0466	4.5	0.0000	0.0
All	0.0884	7.6	0.0000	0.0
		Underhill, VT		
Rain	0.0749	7.2	0.0507	6.6
Snow	0.0722	15.0	0.0508	16.0
Mixed	0.0652	6.1	0.0254	4.5
All	0.0728	7.9	0.0266	4.8

(a) $S_p = \left(\sum_{i=1}^{N} d_i^2/2N\right)^{1/2}$, pooled standard deviation.

(b) $RS_p = S_p/\overline{R}$, where $\overline{R}$ is the average rain gauge measurement.

(c) MACD = median absolute collocated pair difference.

(d) RACD = MACD/median rain gauge depth.

Table 5-12

SEASONAL DIFFERENCES IN RAIN GAUGE BIAS

Season	Kansas			Vermont			Significant Site Diff.[c]
	RD(%)[a]	RSD(%)[b]	N	RD(%)	RSD(%)	N	
Winter	3.0	6.6	13	-8.8	7.5	37	Yes
Spring	0.2	3.0	32	0.6	8.0	36	No
Summer	4.4	13.2	18	-5.5	2.6	27	No
Fall	-0.9	1.5	24	-2.9	8.4	41	No
Sig. Seasonal Diff.[d]	No			Yes			

(a) RD = bias/$\bar{R}$, where $\bar{R}$ is the average rain gauge depth.
(b) RSD = standard deviation of the differences/$\bar{R}$.
(c) Pairwise comparisons based on separate variance t-test.
(d) Significant differences detected by a one-way ANOVA using the Welch test.

collected by the two gauges were detected at the Vermont site. As expected, the differences are greatest in the winter quarter, which contains primarily snow and mixed events. The observed differences at the Vermont site, particularly in the winter, can be attributed in part to the location of the site on a hillside platform, which is subject to more drainage winds down the face of the hill. Snow capture efficiency, especially with high winds, is much worse than that for rain. All but one of the weekly samples in the winter in Vermont were either snow or mixed.

Daily Deposition Sampler Bias and Precision

The bias and precision of the daily deposition data was calculated from the differences between the product of the values of collector 1 and rain gauge 1, and the product of the values of collector 2 and rain gauge 2. Summary statistics for sampler deposition bias and precision are given in Tables 5-13 and 5-14, respectively. For the Kansas site, all the ion biases have a negative sign. This occurs even though rain gauge No. 1 collects 1.1% more precipitation than rain gauge No. 2 (see Table 5-10). For the Vermont site, the ion biases, except for potassium and magnesium, are also negative and are in accord with the rain gauge bias.

Table 5-13 identifies bias values that different significantly from zero, as detected by the Wilcoxon test. Collocated deposition values for all ions except K^+ are significantly different at the Vermont site; this may be attributable to the significant differences in the rain gauge amounts (Table 5-10). No median deposition differences at the Kansas site are significantly different from zero.

Daily deposition precision, using the relative absolute collocated difference (RACD) as the measure, is generally poorer than daily concentration precision (see Table 5-4). This is to be expected since deposition differences are affected by both concentration differences and rain gauge differences. This is not always the case at the Kansas site, however, where the median difference between the two rain gauges is 0 (Table 5-4). At Kansas the daily concentration precision (RACD) is higher than the daily deposition precision for H^+, Ca^{2+}, and Mg^{2+}.

Table 5-13

DAILY DEPOSITION SAMPLER BIAS (mg/l) FOR ALL PRECIPITATION TYPES COMBINED

Analyte	Site	Bias[a]	Std. Dev.	RD (%)[b]	RSD (%)[c]	N
H^+	Kansas	-0.011	0.043	-5.0	19.7	72
	Vermont	-0.032[W]	0.114	-7.0	25.1	127
$SO_4^=$	Kansas	-0.553	2.367	-2.5	10.9	72
	Vermont	-1.185[W]	2.502	-5.8	12.2	125
NO_3^-	Kansas	-0.294	2.339	-1.9	15.3	72
	Vermont	-0.983[W]	2.207	-7.3	16.5	125
NH_4^+	Kansas	-0.145	0.629	-2.7	12.0	72
	Vermont	-0.123[W]	0.897	-4.4	31.8	119
Cl^-	Kansas	-0.068	0.596	-4.5	39.3	72
	Vermont	-0.044[W]	0.232	-5.6	28.4	125
Na^+	Kansas	0.135	0.793	-13.9	82.2	72
	Vermont	-0.027[W]	0.125	-8.7	40.2	115
K^+	Kansas	-0.022	0.141	-4.5	28.6	72
	Vermont	-0.018	0.325	-10.3	183.0	114
CA^{2+}	Kansas	-0.092	1.151	-2.0	24.7	72
	Vermont	-0.028[W]	0.468	-3.3	55.2	114
Mg^{2+}	Kansas	-0.0095	0.080	-2.4	20.2	72
	Vermont	0.014[W]	0.259	9.2	171.0	114

(a) Bias = $\bar{d}$, mean collocated deposition difference.

(b) RD = relative difference, $\bar{d}/\bar{D}$, where $\bar{D}$ is the average daily deposition amount.

(c) RSD = relative standard deviation, standard deviation/$\bar{D}$.

W = Significant deposition bias based on the Wilcoxon signed-rank test.

Table 5-14

DAILY DEPOSITION MEASUREMENT PRECISION (mg/l)

Analyte	Site	S_p[a]	RS_p (%)[b]	MACD[c]	RACD (%)[d]
H^+	Kansas	0.031	14.2	0.007	6.6
	Vermont	0.084	18.3	0.029	14.6
$SO_4^=$	Kansas	1.71	7.9	0.744	5.2
	Vermont	1.95	9.5	0.833	11.6
NO_3^-	Kansas	1.65	10.8	0.46	4.0
	Vermont	1.70	12.6	0.85	12.0
NH_4^+	Kansas	0.45	8.6	0.31	11.1
	Vermont	0.64	22.6	0.11	11.5
Cl^-	Kansas	0.42	27.7	0.10	14.6
	Vermont	0.17	20.3	0.07	17.9
Na^+	Kansas	0.56	58.6	0.28	13.2
	Vermont	0.09	28.8	0.03	32.6
K^+	Kansas	0.10	20.3	0.04	19.5
	Vermont	0.08	45.7	0.02	30.8
Ca^{2+}	Kansas	0.81	17.4	0.21	7.7
	Vermont	0.33	38.9	0.06	23.3
Mg^{2+}	Kansas	0.056	14.2	0.019	9.1
	Vermont	0.18	120.4	0.008	20.5

(a) $S_p = \left(\sum_{i=1}^{N} d_i^2/2N\right)^{1/2}$, pooled standard deviation.

(b) RS_p = relative S_p, $S_p/\overline{D}$, where $\overline{D}$ is the average daily deposition amount.

(c) MACD = median absolute collocated deposition difference.

(d) RACD = MACD/median daily deposition amount.

Annual and Seasonal Deposition

Deposition amounts were calculated for the one-year study period for Kansas and Vermont, and for approximately 11 months for Georgia, by summing both the measured weekly and derived weekly deposition amounts. The averages of the two daily and the two weekly sampler concentrations were used, but only the routine UAPSP rain gauge at each site was used to calculate deposition amounts. This was done to control for rain gauge variability at a given site and to enable assessment of bias in the derived deposition that can be attributed solely to different sampling schedules. The calculated deposition amounts are unadjusted for missing data and are therefore not directly comparable. The missing values generally occur in the daily deposition data. In addition, trace events are included in the measured weekly depositions but not in the daily deposition data. The measured weekly values are therefore a more reliable indication of actual deposition amounts. The total depositions are listed in Table 5-15 for the three sites. Measured weekly and derived weekly deposition values for the four major ions and calcium are plotted on a weekly basis in Appendix C. There is more acidic deposition at the Vermont site than at the Georgia and Kansas sites, as evidenced by the relatively high H^+, $SO_4^=$, and NO_3^- values. Deposition of Na^+ is by far the highest at the Georgia site, while the Kansas site has the highest Ca^{2+} deposition amounts. In general, the daily values are less than the weekly values, but this may be attributable to missing daily data. We are at a loss, however, to explain the very large difference between the daily and weekly totals for Cl^- at the Kansas and Vermont sites.

Daily and weekly derived deposition values calculated separately for each site for each of the four seasons are summarized in Table 5-16. Deposition varies significantly by season, and the seasonal patterns differ by site. For $SO_4^=$, for example, peak values occur in the spring at the Kansas and Georgia sites, but in the summer at the Vermont site. Peak deposition amounts for H^+ occur in the summer at the Vermont and Georgia sites, and in spring at the Kansas site.

REFERENCES

1. W. J. Conover. Practical Nonparametric Statistics, 2nd ed. New York: Wiley, 1980. Chapter 5.

2. D. L. Sisterson, B. E. Wurfel, and B. M. Lesht, "Chemical Differences Between Event and Weekly Precipitation Samples in Northeastern Illinois." Atmos. Environ. Vol. 19, 1985, pp. 1452-1469.

Table 5-15

SITE ANNUAL DEPOSITIONS (mg/m^2) BASED ON DAILY AND WEEKLY MEASUREMENTS[a]

Analyte	Site	Daily	Weekly
H^+	Georgia	17.9	18.6
	Kansas	13.0	13.9
	Vermont	51.9	53.5
$SO_4^=$	Georgia	1188.3	1243.5
	Kansas	1482.8	1719.3
	Vermont	2333.6	2408.7
NO_3^-	Georgia	691.8	744.0
	Kansas	1022.3	1218.7
	Vermont	1647.0	1654.9
NH_4^+	Georgia	211.1	205.4
	Kansas	366.5	413.3
	Vermont	304.5	311.5
Cl^-	Georgia	414.5	323.8
	Kansas	112.5	264.2
	Vermont	97.7	207.6
Na^+	Georgia	225.9	244.7
	Kansas	72.7	71.9
	Vermont	36.5	38.1
K^+	Georgia	47.4	38.5
	Kansas	35.6	43.8
	Vermont	30.9	29.1
Ca^{2+}	Georgia	111.3	124.1
	Kansas	346.4	392.0
	Vermont	85.4	108.0
Mg^{2+}	Georgia	34.4	35.7
	Kansas	28.9	34.3
	Vermont	14.8	18.0

(a) For Georgia the depositions are for approximately 11 months. Deposition amounts are not adjusted for missing weeks.

Table 5-16

SEASONAL DEPOSITIONS (mg/m^2) DERIVED FROM DAILY AND WEEKLY MEASUREMENTS

Analyte		Winter		Spring		Summer		Fall[a]	
		Daily	Weekly	Daily	Weekly	Daily	Weekly	Daily	Weekly
H^+	Georgia	4.8	5.2	5.4	5.2	6.4	6.8	1.2	1.4
	Kansas	0.74	0.92	7.7	8.5	1.5	1.4	3.1	3.0
	Vermont	7.1	8.3	11.5	11.8	21.0	20.1	12.3	13.2
$SO_4^=$	Georgia	273.5	283.8	545.3	565.2	312.3	320.5	57.2	73.8
	Kansas	108.3	105.1	925.7	1053.0	138.5	142.5	310.3	418.7
	Vermont	203.3	200.3	532.0	569.3	1109.1	1075.6	489.2	563.5
NO_3^-	Georgia	139.0	151.1	331.0	350.6	187.0	200.5	34.8	41.8
	Kansas	94.1	108.3	551.5	639.7	164.0	171.5	212.7	299.3
	Vermont	465.3	369.3	306.0	368.6	520.3	508.3	355.6	408.6
NH_4^+	Georgia	30.8	30.7	143.9	135.6	28.5	30.2	7.9	8.9
	Kansas	25.9	26.5	230.8	254.9	34.8	34.4	74.9	97.5
	Vermont	31.8	22.3	64.7	70.6	152.5	148.3	55.5	70.3
Cl^-	Georgia	124.2	78.8	219.1	188.4	37.8	33.9	33.4	22.7
	Kansas	7.5	16.2	61.1	157.5	16.7	25.1	27.3	65.3
	Vermont	35.0	31.7	18.9	44.5	25.0	87.4	18.7	43.9
Na^+	Georgia	64.4	67.8	123.0	132.8	20.3	22.7	18.2	21.4
	Kansas	6.9	7.0	41.9	38.3	8.1	7.7	15.7	18.9
	Vermont	13.7	15.4	7.2	7.9	9.4	8.9	6.3	5.8

Table 5-16 (Concluded)

Analyte		Winter		Spring		Summer		Fall[a]	
		Daily	Weekly	Daily	Weekly	Daily	Weekly	Daily	Weekly
K^+	Georgia	7.7	5.6	33.2	26.0	5.4	5.2	1.1	1.6
	Kansas	2.0	2.4	22.9	22.7	4.5	4.4	6.2	14.2
	Vermont	1.5	2.7	7.2	8.9	17.9	6.7	4.3	10.8
Ca^{2+}	Georgia	18.7	20.6	71.1	81.6	17.8	17.4	3.6	4.5
	Kansas	29.3	29.9	200.7	212.2	53.3	52.5	63.0	97.5
	Vermont	15.3	12.4	22.2	36.1	34.3	32.8	13.7	26.7
Mg^{2+}	Georgia	8.4	8.7	19.9	20.5	3.7	2.4	2.8	-17.9
	Kansas	2.7	2.9	16.7	18.4	4.3	2.3	5.1	8.7
	Vermont	2.2	2.4	3.4	5.4	6.8	20.3	2.4	4.8

(a) The fall data combine 1983 and 1984 measurements. For Georgia sampling occurred only in October and November. Deposition amounts are not adjusted for missing weeks.

3. L. E. Topol and R. Schwall. "Precipitation Chemistry Measurements in the SURE Region." Draft Final Report. Palo Alto, CA: Electric Power Research Institute, 1986.

4. L. E. Topol and R. Schwall. "The Utility Acid Precipitation Study Program, Network Description and Measurements for 1981-1982." UAPSP report 105. Washington, DC: Utility Acid Precipitation Study Program, 1986.

Section 6

CONCLUSIONS

The study described in this report compared the results of weekly and daily precipitation samples. The following conclusions were drawn from the analyses:

- The collection efficiencies were highest for rain and about equal for snow and mixed precipitation with a value of about 1.1 for rain and 0.75 for mixed and snow. Generally small differences were observed between weekly and daily sampling and among sites for the same precipitation type.

- The precision of ionic conentration determinations is either comparable or better for daily than for weekly samples. Overall measurement precision for both sampling protocols (with the exception of K^+) is less than 20 percent of ionic concentrations.

- The measured weekly concentrations were, in most cases, approximately 10 percent higher than the weekly concentrations derived from daily samples.

- The differences between weekly and composited daily concentrations varied by constituents, but they were in general less than 10 percent of the mean concentration. Also, the individual ion concetration biases are of similar magnitudes and direction among the sites with the exception of H^+ and Na^+.

- There is seasonal variation in the concentration bias between daily composited and weekly samples. Concentrations of all ions except NH_4^+ were significantly higher in the fall for the weekly measurements. Concentrations of Ca^{2+} and NO_3^- were significantly higher in weekly measurements in the spring. No statistically significant biases were observed for the summer quarter.

- Differences in paired rain gauge depths at the two sites with collocated rain gauges were greatest for snow samples. Overall, paired rain gauges at the Vermont site measured significantly different precipitation amounts; the differences were greatest in the winter quarter, when there was more blow-away of

snow. The significant differences in rain gauge depth resulted in significant differences in daily deposition for all ions except K^+ at the Vermont site.

- Precision of daily depositions (calculated from the two daily collectors and the two rain gauges) was better at the Kansas site; for most ions the precision was 5 to 15 percent. At the Vermont site, where the rain gauge differences were larger, the precision of ion depositions were 10 to 30 percent (as measured by relative absolute collocted difference).

- Calculated deposition amounts vary by season at each site. Peak $SO_4^=$ deposition occurred in the spring at the Kansas and Georgia sites, and in the summer at the Vermont site. Peak H^+ deposition values occurred in the summer at the Vermont and Georgia sites, and in the spring at the Kansas site.

The conclusions of this study favor daily sampling over weekly sampling to detect trends in concentration or deposition more readily. Our conclusions indicate that, for most ions, weekly samples yield higher concentrations than daily samples. Therefore, a network that changes its sampling schedule would see a bias that interferes with trend analysis. Also, comparison of concentrations from networks with different sampling collection schedules will be influenced by these biases. Finally, the seasonal differences in deposition strongly favor monitoring and data analysis for a whole year and preferably for complete seasons.

Additional analysis remains to be done on three items. First, it is not known how the exclusion of trace events from the daily concentration data would alter the method bias. It has been suggested that ionic concentrations are particularly high in trace events. We can compare the measured and derived concentrations for only those weeks where no trace events occurred. Second, deposition method bias remains to be estimated. Calculated annual deposition amounts presented in this report were unadjusted for missing data (trace samples or partial samples) in the daily measurements. Deposition method bias can be calculated by comparing measured and derived weekly deposition values for only those weeks where there are no missing concentrations. Third, the sensitivity of results to different outlier rejection schemes is unknown. Those results based on nonparametric techniques applied to the unscreened data (i.e., no outliers removed) would not be affected. But precision, as measured by the pooled standard deviation, can be significantly altered by choice of outliers rejected. The results of these tasks should provide additional insight into the comparability of daily and weekly precipitation chemistry measurements.

Appendix A

WEEKLY AND DAILY SAMPLER BIAS SUMMARY STATISTICS BY PRECIPITATION TYPE

Appendix A

BASIC SUMMARY STATISTICS

Sampler concentration bias, estimated by the average collocated difference, is examined in Section 5; relative bias estimates and standard deviations are presented in Table 5-3 for all precipitation types combined. In this Appendix, we list relative sampler concentration bias and standard deviation by precipitation type at each site. Statistical significance of the reported biases is tested with the Wilcoxon signed-rank test; those biases which are significant are noted in the tables.

Table A-1

RELATIVE PERCENT DIFFERENCES (RPD) AND RELATIVE STANDARD DEVIATIONS (RSD) FOR COLLOCATED RAIN SAMPLES IN UVALDA, GA

	Daily Sampling			Weekly Sampling		
Analyte	RD (%)[a]	RSD (%)[b]	N	RD (%)	RSD (%)	N
Precip	-1.7[W]	3.9	63	-0.0	9.2	34
H^+	-4.1	12.2	57	0.0	17.4	32
$SO_4^=$	-2.4[W]	5.9	57	0.0	13.6	32
NO_3^-	-2.8[W]	5.4	57	-4.5	22.5	32
NH_4^+	-3.3	21.3	57	-2.9	46.3	32
Cl^-	-0.8[W]	13.0	57	1.8	8.3	32
Na^+	-2.8[W]	14.0	57	1.3	17.2	32
K^+	-7.0	58.8	57	-2.8	30.6	32
Ca^{2+}	-2.7	21.7	57	1.5	15.0	32
Mg^{2+}	0.0	18.5	57	-2.3	11.8	32

(a) RD = $(\bar{d}/\bar{C}) \times 100$, where $\bar{d}$ and $\bar{C}$ are the mean collocated difference and average concentration.

(b) RSD = $(S_d/\bar{C}) \times 100$, where S_d is the standard deviation of the collocated differences.

W = Sampler bias for the collocated pair significantly different from zero based on the Wilcoxon signed-ranks test.

Table A-2

RELATIVE PERCENT DIFFERENCES (RD) AND RELATIVE STANDARD DEVIATIONS (RSD) FOR COLLOCATED SAMPLES IN LANCASTER, KS

	Daily Sampling			Weekly Sampling		
Analyte	RD (%)[a]	RSD (%)[b]	N	RD (%)	RSD (%)	N
			Rain			
Precip	-1.3[W]	3.6	60	0.2	1.3	24
H^+	-6.1	18.2	58	7.1	21.4	23
$SO_4^=$	-0.6	9.4	58	-3.1	11.1	23
NO_3^-	-0.9	10.0	58	-2.2	11.1	23
NH_4^+	-5.5[W]	13.8	58	-1.7	17.5	23
Cl^-	-6.5	36.6	58	-0.8	14.2	23
Na^+	-7.6	32.9	58	-4.0	12.0	23
K^+	-5.9[W]	23.5	58	2.4	43.9	23
Ca^{2+}	1.1	9.0	58	-3.9	19.9	23
Mg^{2+}	2.2	15.2	58	-4.5	27.3	23
			Snow			
Precip	-18.4	9.6	4	14.8	11.1	4
H^+	15.4	19.2	4	2.3	4.5	4
$SO_4^=$	-19.8	17.7	4	-8.3	25.4	4
NO_3^-	-4.2	5.1	4	0.9	5.5	4
NH_4^+	-45.2	59.7	4	-36.8	87.6	4
Cl^-	23.3	38.6	4	-5.5	15.1	4
Na^+	6.3	37.5	4	43.5	60.9	4
K^+	120	193	4	-88.9	111	4
Ca^{2+}	-7.8	5.0	4	-11.2	39.2	4
Mg^{2+}	0.0	22.8	4	-26.7	46.7	4

Table A-2 (Concluded)

	Daily Sampling			Weekly Sampling		
Analyte	RD (%)[a]	RSD (%)[b]	N	RD (%)	RSD (%)	N
			Mixed			
Precip	0.8	12.9	8	0.5	7.6	8
H^+	-13.8	82.8	8	25.0	56.2	8
$SO_4^=$	-14.7[W]	16.5	8	-1.6	5.7	8
NO_3^-	6.6	58.8	8	-0.7	9.4	8
NH_4^+	-16.2	33.1	8	0.7	1.1	8
Cl^-	-15.2	70.4	8	-14.3	36.6	8
Na^+	-36.8	61.7	8	0.0	17.4	8
K^+	-22.9	110	8	-39.7	115	8
Ca^{2+}	-3.3	42.7	8	-14.9	26.7	8
Mg^{2+}	-9.0	36.0	8	32.3	73.1	8

(a) RD = $(\overline{d}/\overline{C})$ x 100, where $\overline{d}$ and $\overline{C}$ are the mean collocated difference and average concentration.

(b) RSD = $(S_d/\overline{C})$ x 100, where S_d is the standard deviation of the collocated differences.

W = Sampler bias for the collocated pair significantly different from zero based on the Wilcoxon signed-ranks test.

Table A-3

RELATIVE PERCENT DIFFERENCES (RD) AND RELATIVE STANDARD DEVIATIONS (RSD) FOR COLLOCATED SAMPLES IN UNDERHILL, VT

	Daily Sampling			Weekly Sampling		
Analyte	RD (%)[a]	RSD (%)[b]	N	RD (%)	RSD (%)	N
			Rain			
Precip	-0.6	2.8	81	-0.6	3.6	26
H^+	0.0	9.1	77	-3.9	11.8	24
$SO_4^=$	-0.2	3.8	76	-1.5	4.7	24
NO_3^-	-0.5	5.2	76	-2.6	8.0	24
NH_4^+	-3.7	21.8	76	1.9	16.4	24
Cl^-	-0.9	19.9	76	-4.9	19.6	24
Na^+	-4.8	24.0	75	-12.2	31.7	24
K^+	-3.3	52.5	76	-4.2	133	24
Ca^{2+}	-0.7	8.9	75	3.0	16.7	24
Mg^{2+}	0.0	16.0	75	4.3	26.1	24
			Snow			
Precip	-9.6^W	10.3	27	2.3	7.3	4
H^+	-1.9^W	5.7	25	-1.7	7.0	4
$SO_4^=$	-2.4	9.9	24	-1.7	6.9	4
NO_3^-	0.4	4.2	24	-1.4	7.2	4
NH_4^+	2.5	12.7	21	9.1	14.6	4
Cl^-	-3.4	12.8	24	-2.2	13.8	4
Na^+	-7.9	18.4	20	1.6	3.2	3
K^+	-21.0	52.6	20	0.0	13.8	3
Ca^{2+}	2.0	19.6	20	3.3	6.7	3
Mg^{2+}	0.0	15.4	20	0.0	1.0	3

Table A-3 (Concluded)

	Daily Sampling			Weekly Sampling		
Analyte	RD (%)[a]	RSD (%)[b]	N	RD (%)	RSD (%)	N
			Mixed			
Precip	-1.6[W]	6.3	24	3.2[W]	3.1	17
H^+	-2.2	8.6	24	2.6	12.8	17
$SO_4^=$	-1.7	6.5	24	3.7	12.8	16
NO_3^-	-0.8	6.1	24	3.1	10.5	16
NH_4^+	0.5	11.8	24	0.6	9.5	15
Cl^-	-2.2	39.3	24	5.6	14.2	16
Na^+	-9.8	36.0	23	8.7	26.1	16
K^+	4.9	29.3	23	0.0	29.4	16
Ca^{2+}	-12.5[W]	26.3	22	2.4	16.9	15
Mg^{2+}	-8.7	26.1	22	8.7	17.4	15

(a) RD = $(\overline{d}/\overline{C})$ x 100, where $\overline{d}$ and $\overline{C}$ are the mean collocated difference and average concentration.

(b) RSD = $(S_d/\overline{C}$ x 100, where S_d is the standard deviation of the collocated differences.

W = Sampler bias for the collocated pair significantly different from zero based on the Wilcoxon signed-ranks test.

Appendix B

WEEKLY MEASURED AND DERIVED WEEKLY ANALYTE CONCENTRATIONS FOR EACH SITE AND PRECIPITATION TYPE

Appendix B

CONCENTRATION STATISTICS

Mean and median ionic concentrations are listed for each site in Table 5-5 for all precipitation types combined. In this Appendix, mean and median concentrations are listed by precipitation type (rain, snow, and mixed) at each site. These tables allow a comparison of mean and median concentrations as well as a comparison of derived and measured weekly concentrations.

Table B-1

ANALYTE CONCENTRATIONS (mg/l) IN RAIN FOR WEEKLY MEASURED AND WEEKLY DERIVED SAMPLES

	Measured Weekly			Derived Weekly		
Analyte	Median	Mean	SEM[a]	Median	Mean	SEM
			Uvalda, GA			
Precip (grams)	1832	2312	330	1848	2362	326
pH (pH units)	4.84	4.65	0.07	4.87	4.65	0.06
H^+	0.015	0.023	0.004	0.014	0.022	0.004
$SO_4^=$	1.132	1.329	0.155	0.951	1.261	0.161
NO_3^-	0.628	0.802	0.102	0.627	0.772	0.100
NH_4^+	0.117	0.175	0.026	0.125	0.175	0.027
Cl^-	0.304	0.415	0.055	0.302	0.398	0.057
Na^+	0.212	0.241	0.032	0.156	0.220	0.032
K^+	0.030	0.031	0.005	0.030	0.034	0.007
Ca^{2+}	0.088	0.114	0.020	0.065	0.093	0.017
Mg^{2+}	0.029	0.035	0.005	0.026	0.032	0.005
			Lancaster, KS			
Precip (grams)	1147	1690	377	975	1650	423
pH (pH units)	5.06	4.84	0.08	5.02	4.88	0.07
H^+	0.0088	0.015	0.003	0.0096	0.013	0.002
$SO_4^=$	1.722	1.808	0.169	1.421	1.696	0.188
NO_3^-	1.340	1.396	0.113	1.325	1.349	0.120
NH_4^+	0.383	0.451	0.050	0.359	0.441	0.051
Cl^-	0.100	0.112	0.013	0.124	0.117	0.014
Na^+	0.057	0.061	0.008	0.055	0.062	0.009
K^+	0.035	0.039	0.006	0.036	0.040	0.007
Ca^{2+}	0.416	0.501	0.069	0.439	0.511	0.075
Mg^{2+}	0.035	0.040	0.005	0.035	0.040	0.005

Table B-1 (Concluded)

	Measured Weekly			Derived Weekly		
Analyte	Median	Mean	SEM[a]	Median	Mean	SEM
			Underhill, VT			
Precip (grams)	1096	1559	292	1073	1561	293
pH (pH units)	4.29	4.29	0.05	4.28	4.25	0.05
H^+	0.052	0.051	0.006	0.052	0.056	0.006
$SO_4^=$	2.410	2.653	0.359	2.107	2.744	0.379
NO_3^-	1.185	1.474	0.175	1.285	1.509	0.186
NH_4^+	0.284	0.359	0.069	0.271	0.372	0.082
Cl^-	0.065	0.102	0.030	0.063	0.110	0.035
Na^+	0.019	0.041	0.016	0.017	0.047	0.019
K^+	0.014	0.024	0.005	0.015	0.019	0.004
Ca^{2+}	0.066	0.132	0.042	0.052	0.129	0.046
Mg^{2+}	0.009	0.023	0.006	0.008	0.021	0.007

(a) Standard error of the mean = SD/√N.

Table B-2

ANALYTE CONCENTRATIONS (mg/l) IN SNOW FOR WEEKLY MEASURED AND WEEKLY DERIVED SAMPLES

	Measured Weekly			Derived Weekly		
Analyte	Median	Mean	SEM[a]	Median	Mean	SEM
			Lancaster, KS			
Precip (grams)	157	186	62	156	178	84
pH (pH units)	4.62	4.58	0.09	4.68	4.58	0.11
H^+	0.024	0.026	0.006	0.021	0.026	0.008
$SO_4^=$	0.444	0.503	0.110	0.381	0.474	0.142
NO_3^-	2.247	2.555	0.653	2.090	2.663	0.957
NH_4^+	0.259	0.285	0.089	0.219	0.275	0.078
Cl^-	0.063	0.073	0.025	0.085	0.099	0.044
Na^+	0.010	0.012	0.005	0.016	0.016	0.003
K^+	0.033	0.027	0.007	0.012	0.027	0.018
Ca^{2+}	0.134	0.143	0.036	0.190	0.181	0.059
Mg^{2+}	0.017	0.015	0.004	0.017	0.014	0.004
			Underhill, VT			
Precip (grams)	356	408	159	322	409	166
pH (pH units)	4.21	4.24	0.12	4.19	4.24	0.13
H^+	0.061	0.058	0.016	0.064	0.058	0.017
$SO_4^=$	0.642	0.859	0.210	0.677	0.799	0.162
NO_3^-	3.508	3.221	1.070	3.438	3.203	1.130
NH_4^+	0.110	0.164	0.053	0.084	0.126	0.039
Cl^-	0.152	0.181	0.044	0.153	0.177	0.045
Na^+	0.066	0.062	0.017	0.060	0.060	0.017
K^+	0.014	0.015	0.003	0.010	0.010	0.002
Ca^{2+}	0.057	0.060	0.012	0.036	0.042	0.010
Mg^{2+}	0.005	0.010	0.003	0.006	0.008	0.002

(a) Standard error of the mean = SD/√N.

Table B-3

ANALYTE CONCENTRATIONS (mg/l) IN MIXED (SNOW & RAIN) WEEKLY
MEASURED AND WEEKLY DERIVED SAMPLES

	Measured Weekly			Derived Weekly		
Analyte	Median	Mean	SEM[a]	Median	Mean	SEM
			Lancaster, KS			
Precip (grams)	1602	1758	510	1543	1742	485
pH (pH units)	4.85	4.80	0.13	4.70	4.66	0.12
H^+	0.014	0.016	0.005	0.020	0.022	0.006
$SO_4^=$	2.020	2.283	0.436	1.947	2.280	0.429
NO_3^-	1.405	1.640	0.249	1.334	1.582	0.269
NH_4^+	0.559	0.595	0.099	0.475	0.622	0.103
Cl^-	0.142	0.140	0.029	0.105	0.139	0.033
Na^+	0.053	0.069	0.018	0.056	0.074	0.019
K^+	0.040	0.081	0.030	0.036	0.058	0.018
Ca^{2+}	0.397	0.521	0.115	0.415	0.445	0.089
Mg^{2+}	0.035	0.047	0.010	0.035	0.039	0.008
			Underhill, VT			
Precip (grams)	1674	1761	252	1824	1816	257
pH (pH units)	4.60	4.46	0.09	4.59	4.42	0.09
H^+	0.025	0.035	0.007	0.026	0.038	0.008
$SO_4^=$	0.862	1.284	0.260	0.917	1.273	0.273
NO_3^-	0.896	1.379	0.316	0.970	1.690	0.415
NH_4^+	0.103	0.170	0.044	0.112	0.186	0.046
Cl^-	0.057	0.071	0.016	0.066	0.090	0.024
Na^+	0.024	0.023	0.004	0.025	0.023	0.005
K^+	0.011	0.015	0.003	0.006	0.012	0.003
Ca^{2+}	0.050	0.087	0.028	0.034	0.064	0.017
Mg^{2+}	0.008	0.012	0.003	0.006	0.008	0.002

(a) Standard error of the mean = SD/$\sqrt{N}$.

Appendix C

WEEK-BY-WEEK COMPARISON OF DEPOSITION AMOUNTS CALCULATED FROM DAILY AND WEEKLY SAMPLERS FOR MAJOR IONS (H^+, $SO_4^=$, NO_3^-, NH_4^+, Ca^{2+})

Appendix C

WEEK-BY-WEEK PLOTS OF DEPOSITION

In this appendix we present week-by-week deposition of H^+, $SO_4^=$, NO_3^-, NH_4^+, and Ca^{2+} as calculated from the daily and weekly measurements at each site. The plots show seasonal variation in deposition for these major ions. Weekly deposition values are derived from the daily data by summing the daily deposition amounts. Some deposition amounts are missing from the daily samples but not from the weekly samples because individual trace events (which may contain relatively high ionic concentrations) were not chemically analyzed. Since the derived weekly deposition amounts are not adjusted for the missing events, the derived and measured weekly deposition values are not directly comparable. However, large differences seem to occur only rarely.

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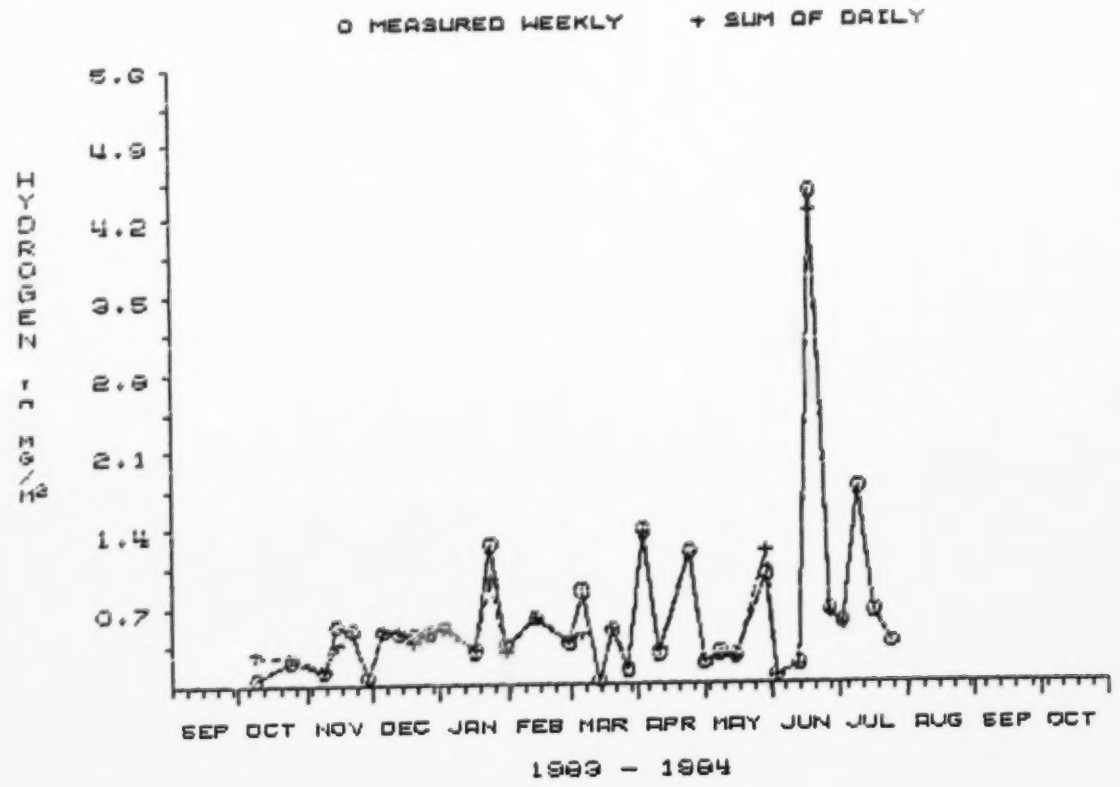

FIGURE C-1. Comparison of measured weekly and composited daily hydrogen deposition for Uvalda, Georgia.

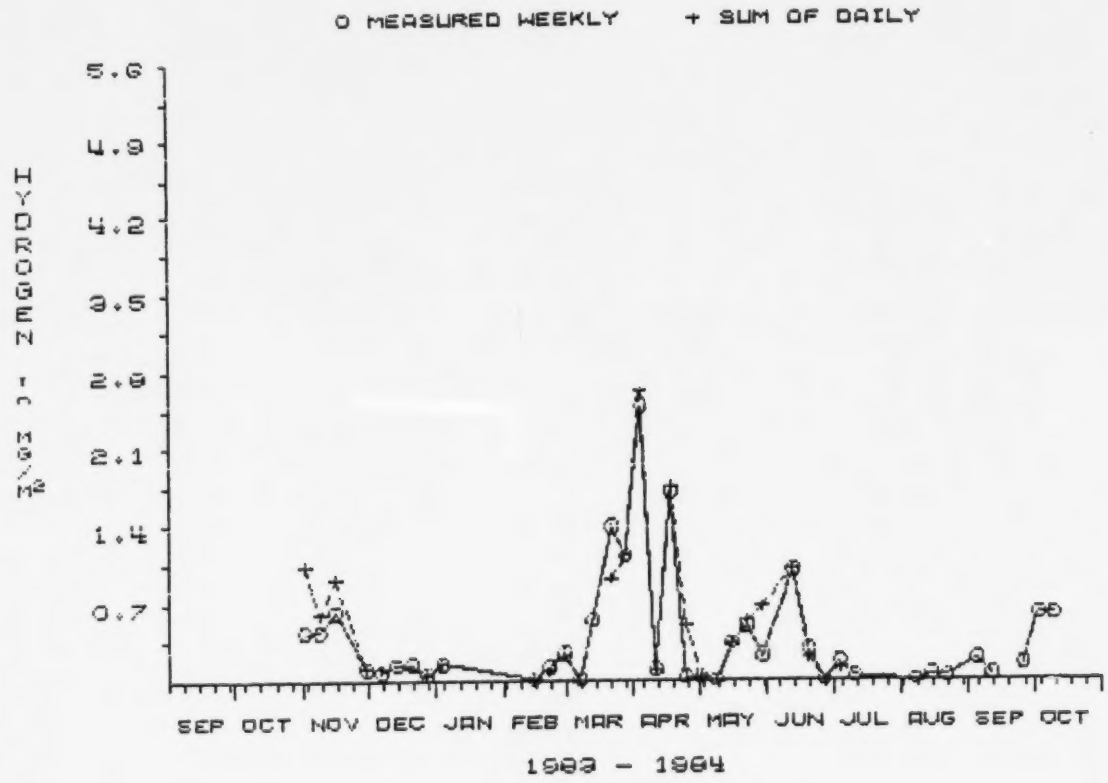

FIGURE C-2. Comparison of measured weekly and composited daily hydrogen deposition for Lancaster, Kansas.

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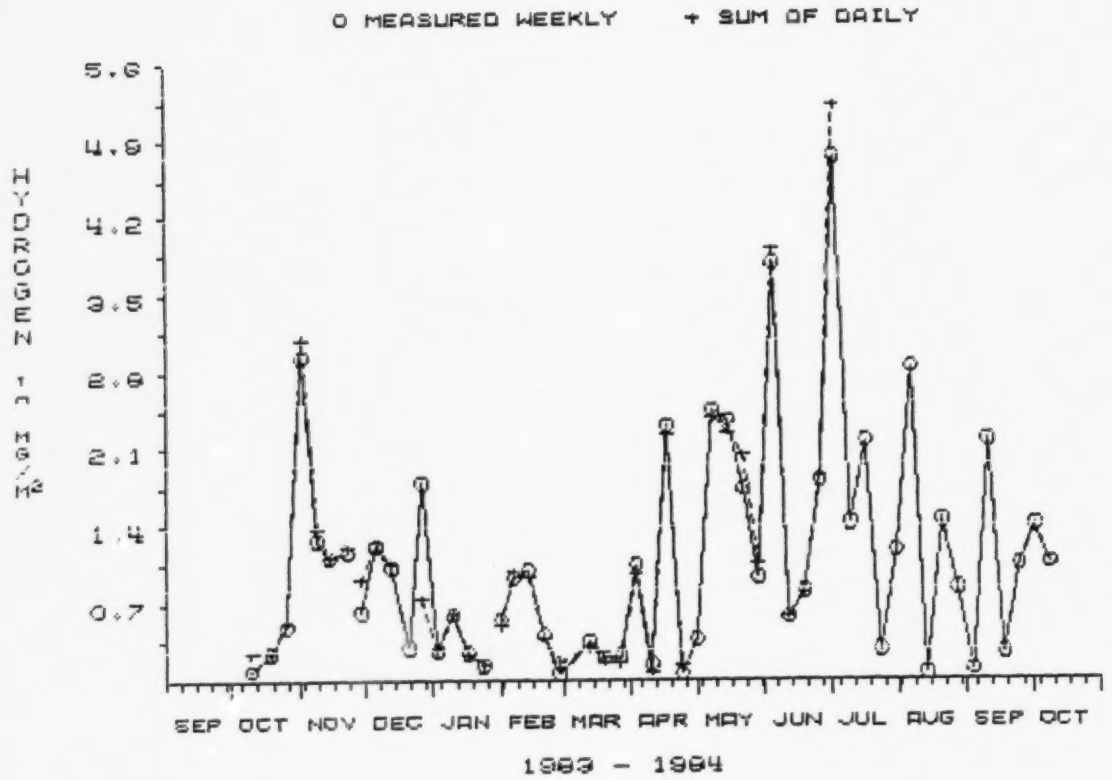

FIGURE C-3. Comparison of measured weekly and composited daily hydrogen deposition for Underhill, Vermont.

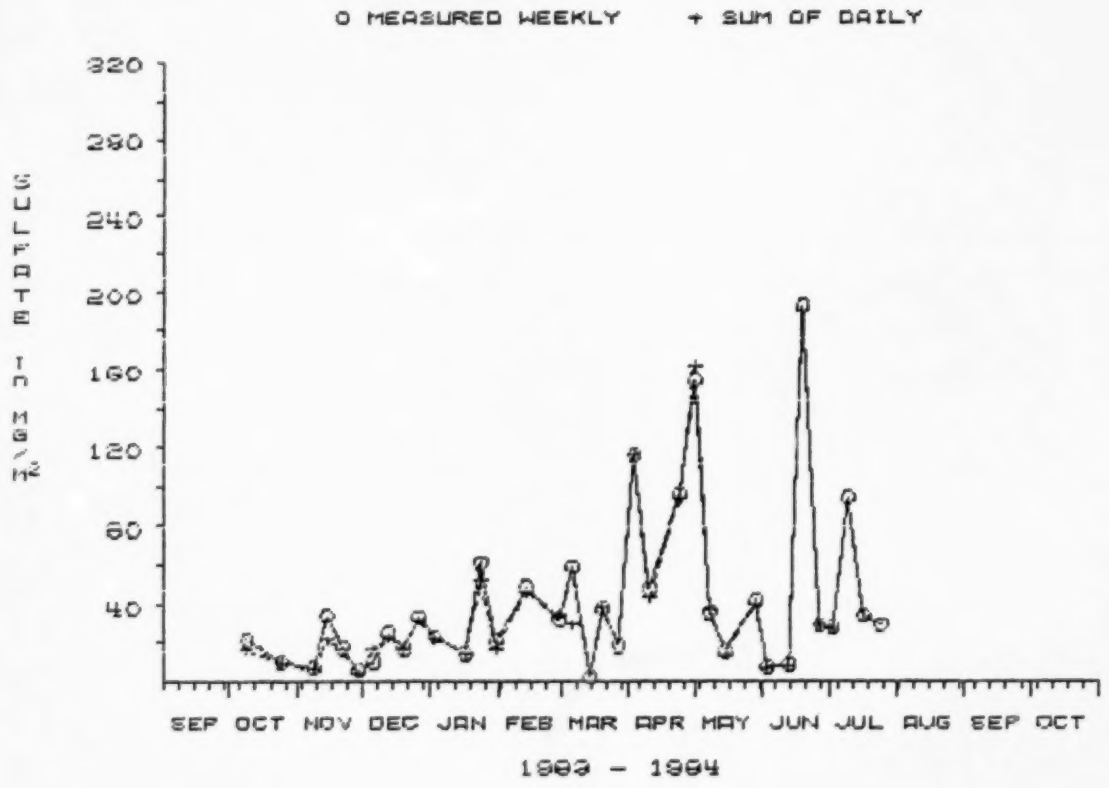

FIGURE C-4. Comparison of measured weekly and composited daily sulfate deposition for Uvalda, Georgia.

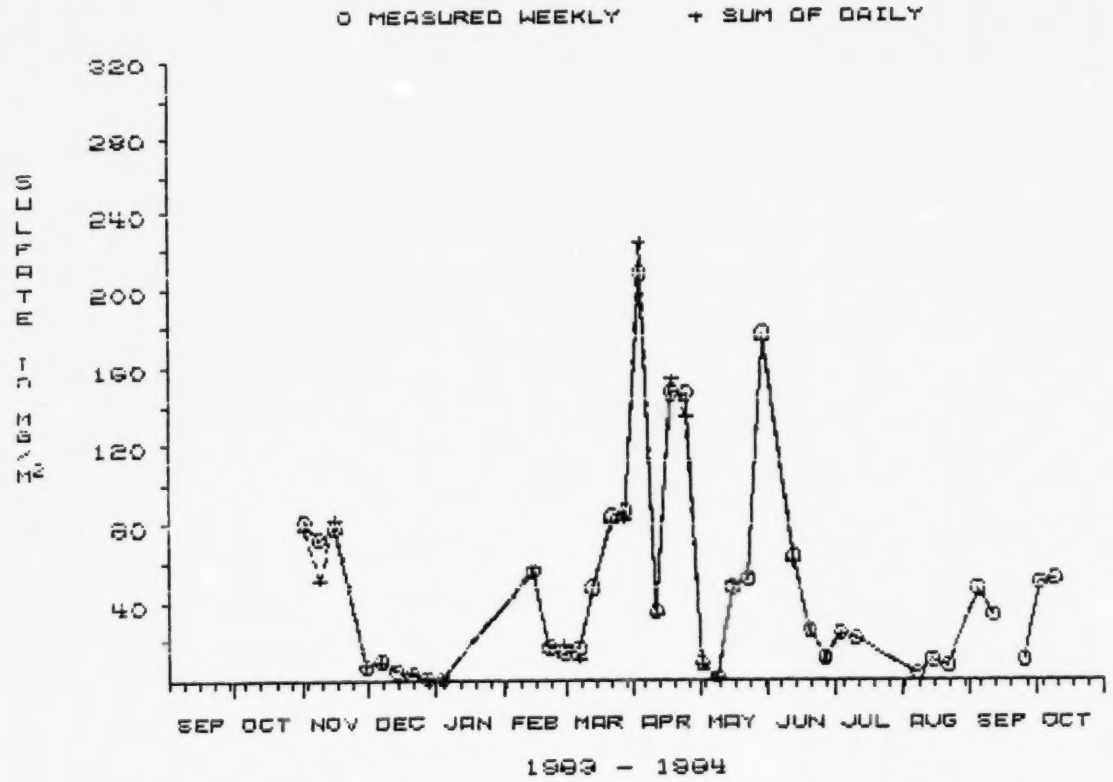

FIGURE C-5. Comparison of measured weekly and composited daily sulfate deposition for Lancaster, Kansas.

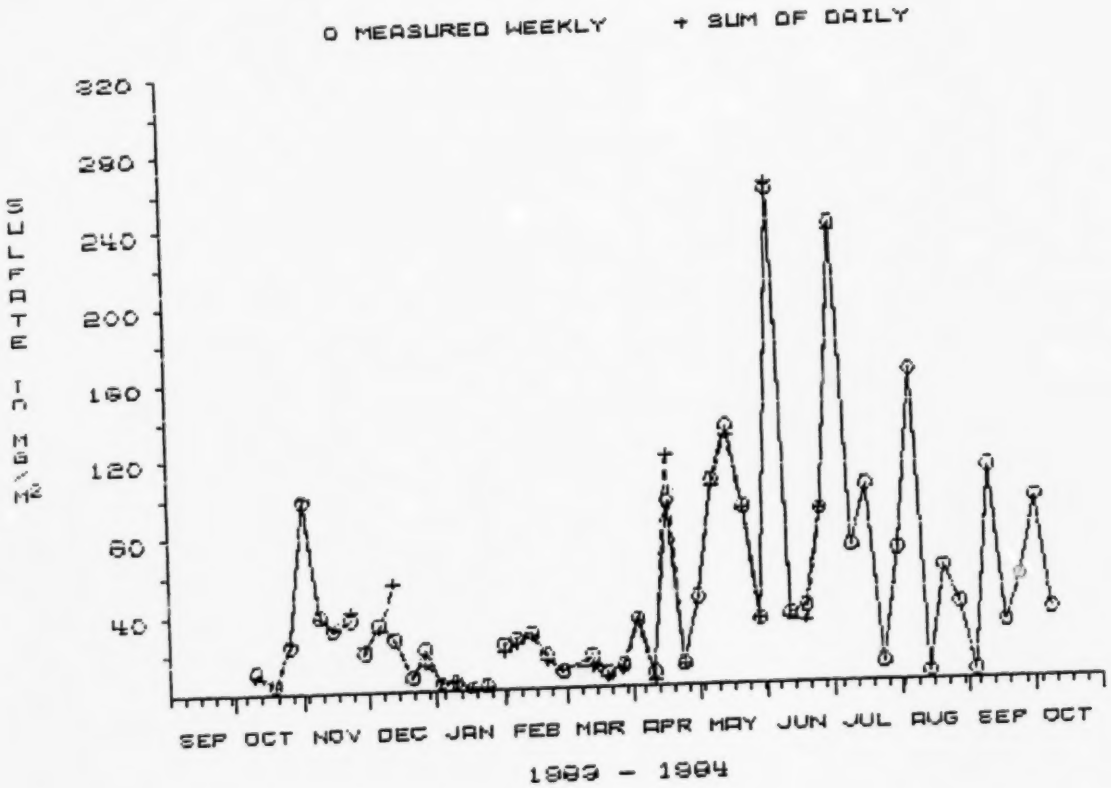

FIGURE C-6. Comparison of measured weekly and composited daily sulfate deposition for Underhill, Vermont.

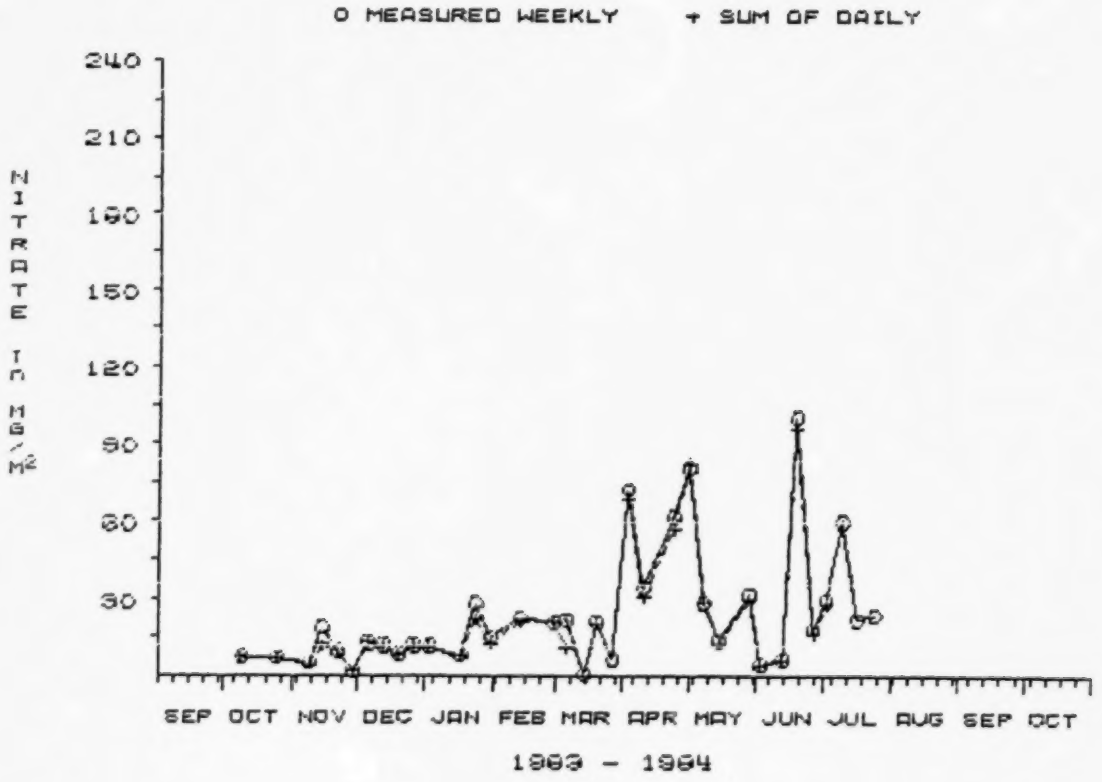

FIGURE C-7. Comparison of measured weekly and composited daily nitrate deposition for Uvalda, Georgia.

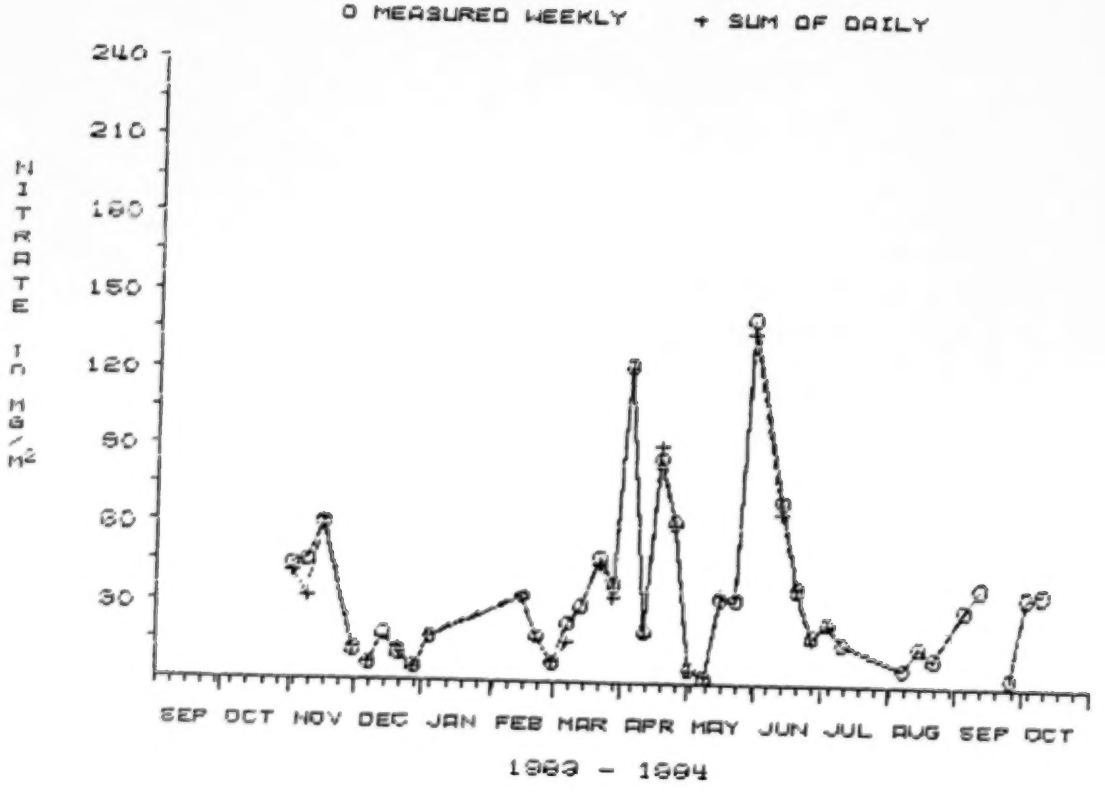

FIGURE C-8. Comparison of measured weekly and composited daily nitrate deposition for Lancaster, Kansas.

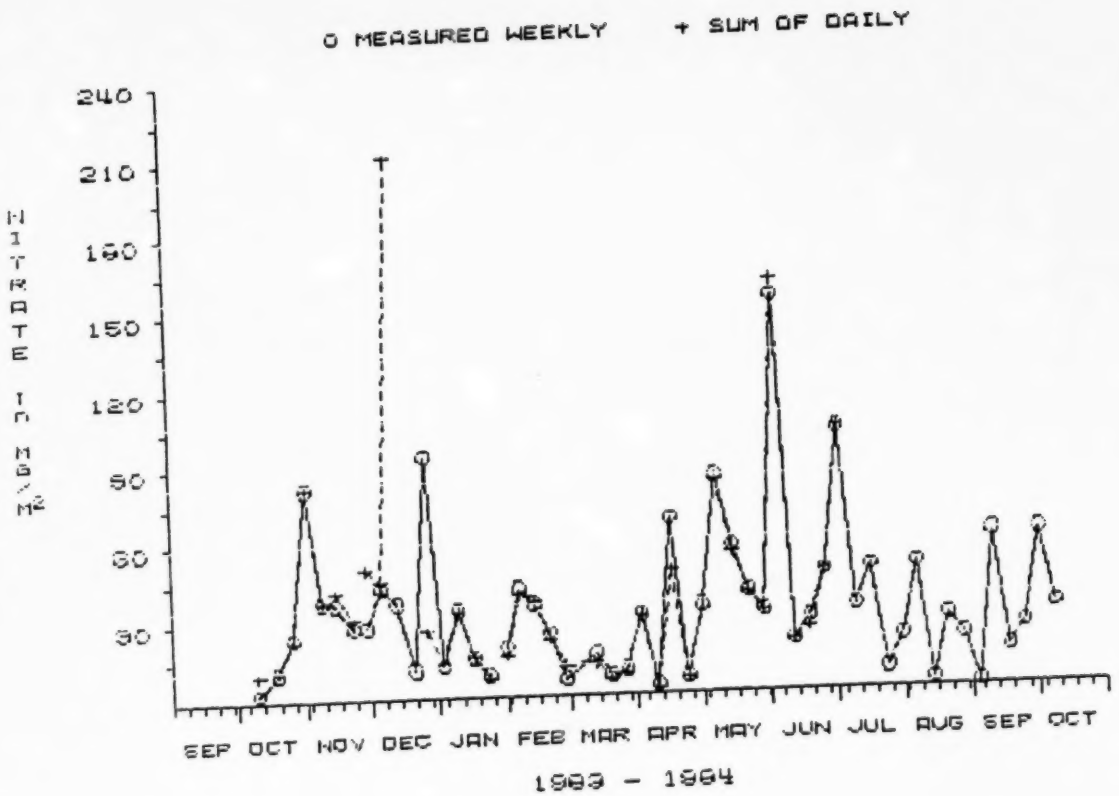

FIGURE C-9. Comparison of measured weekly and composited daily nitrate deposition for Underhill, Vermont.

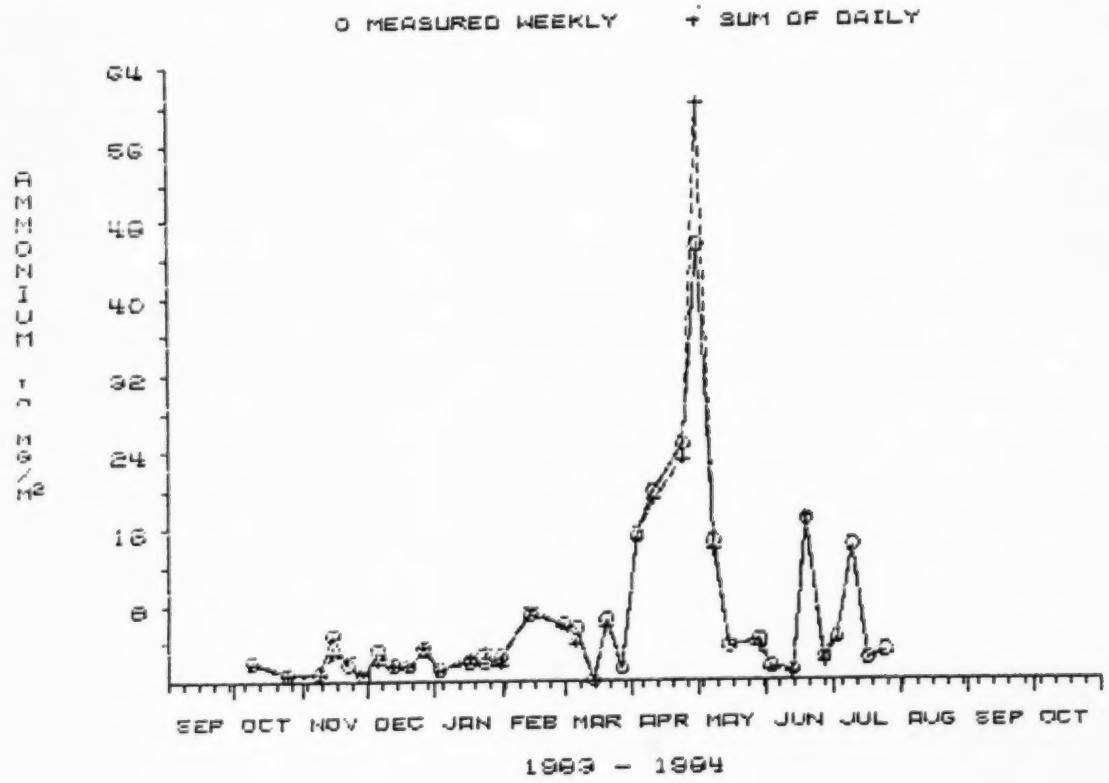

FIGURE C-10. Comparison of measured weekly and composited daily ammonium deposition for Uvalda, Georgia.

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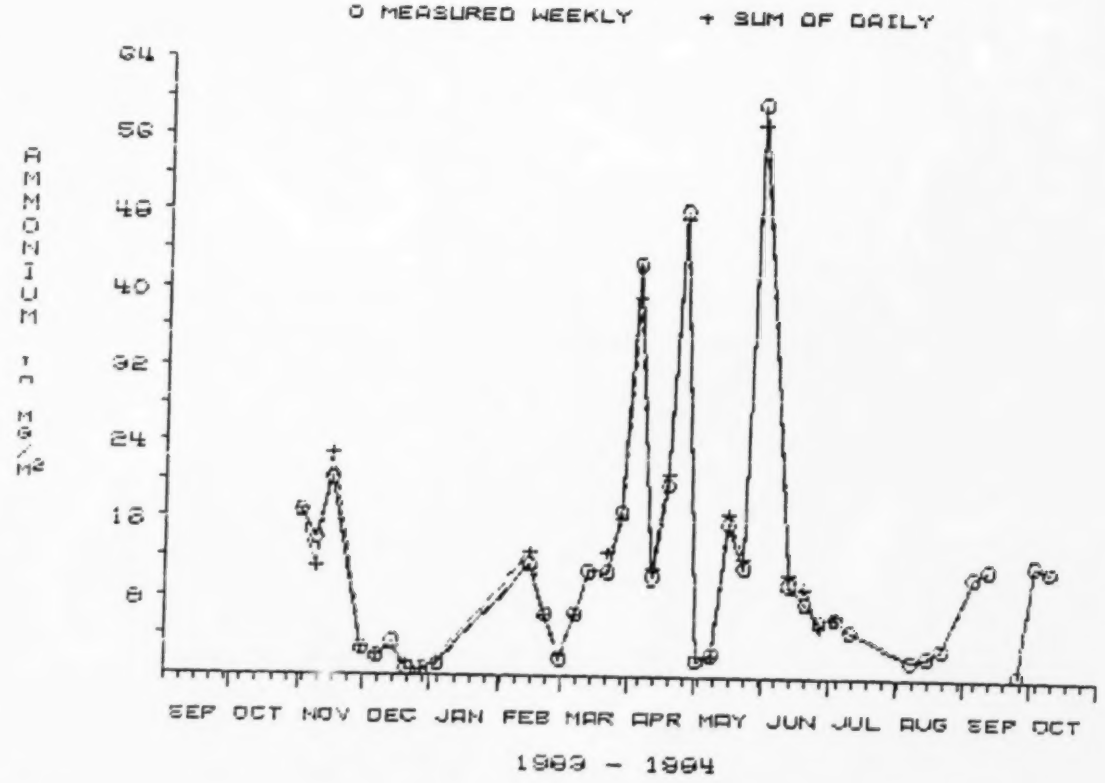

FIGURE C-11. Comparison of measured weekly and composited daily ammonium deposition for Lancaster, Kansas.

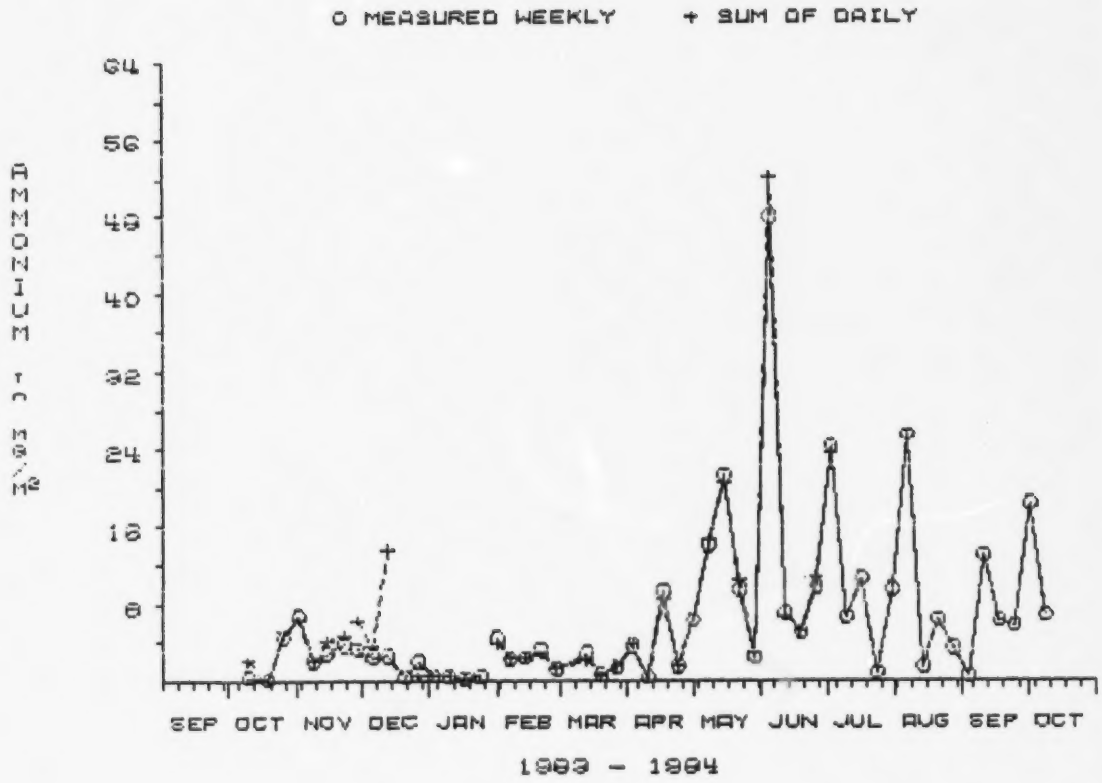

FIGURE C-12. Comparison of measured weekly and composited daily ammonium deposition for Underhill, Vermont.

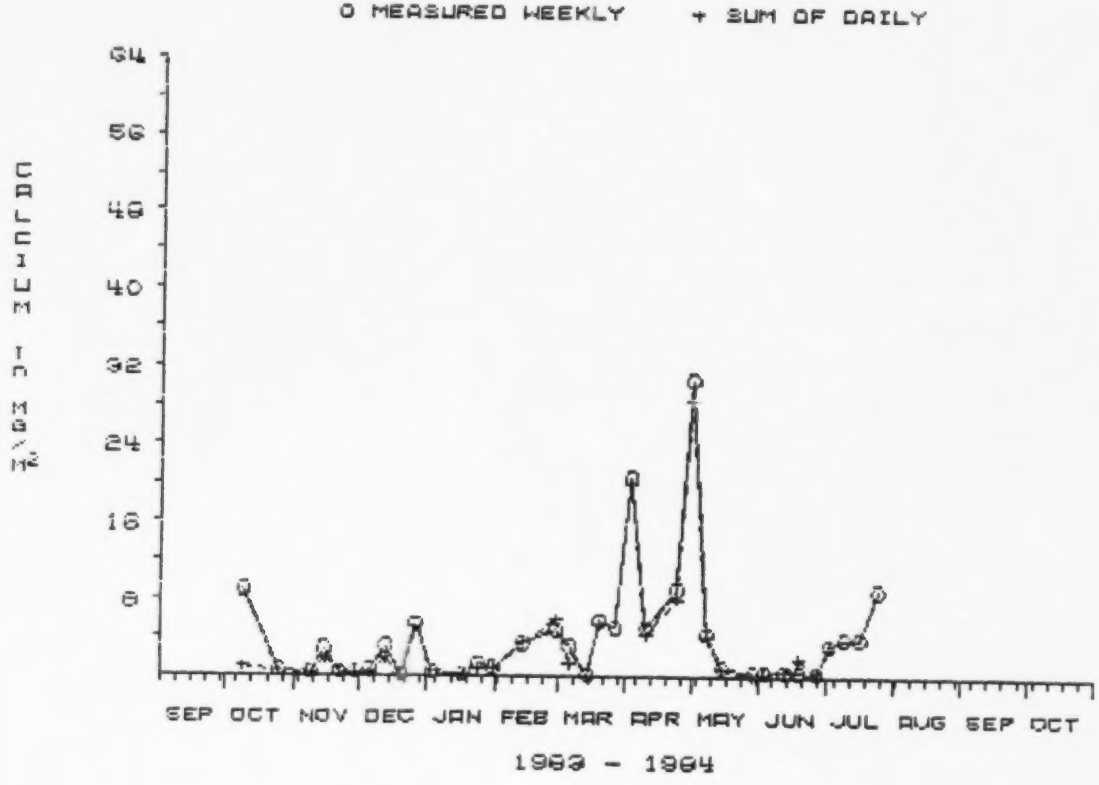

FIGURE C-13. Comparison of measured weekly and composited daily calcium deposition for Uvalda, Georgia.

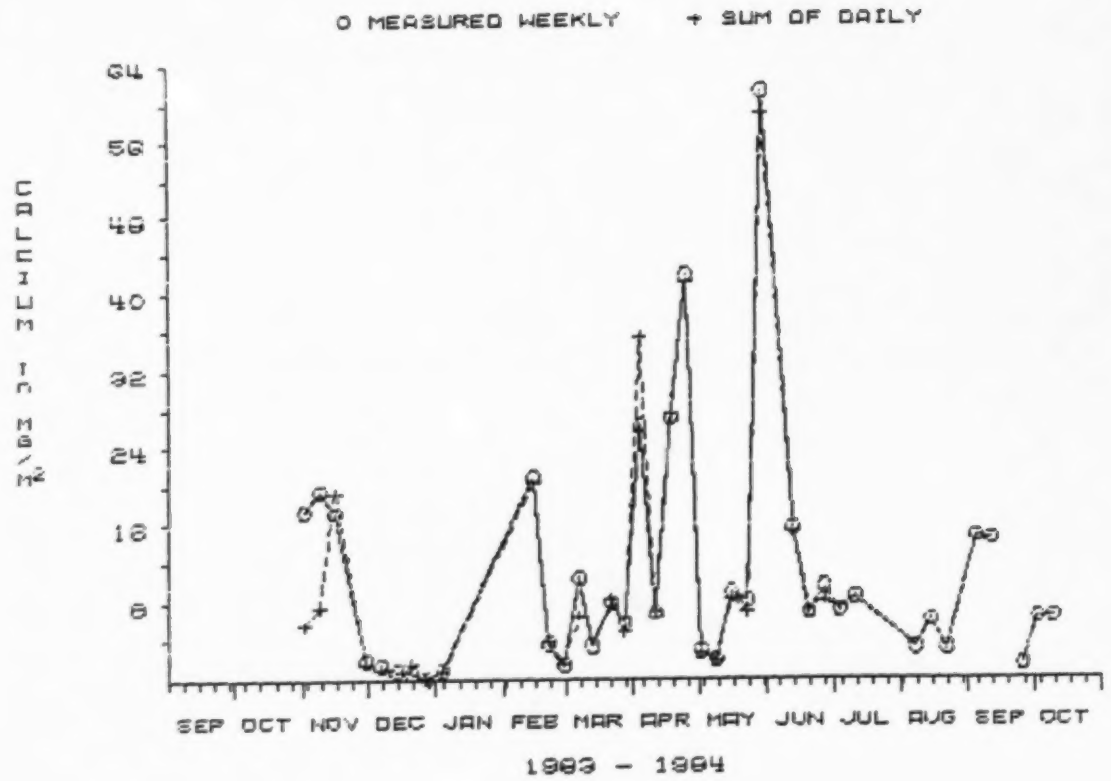

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FIGURE C-14. Comparison of measured weekly and composited daily calcium deposition for Lancaster, Kansas.

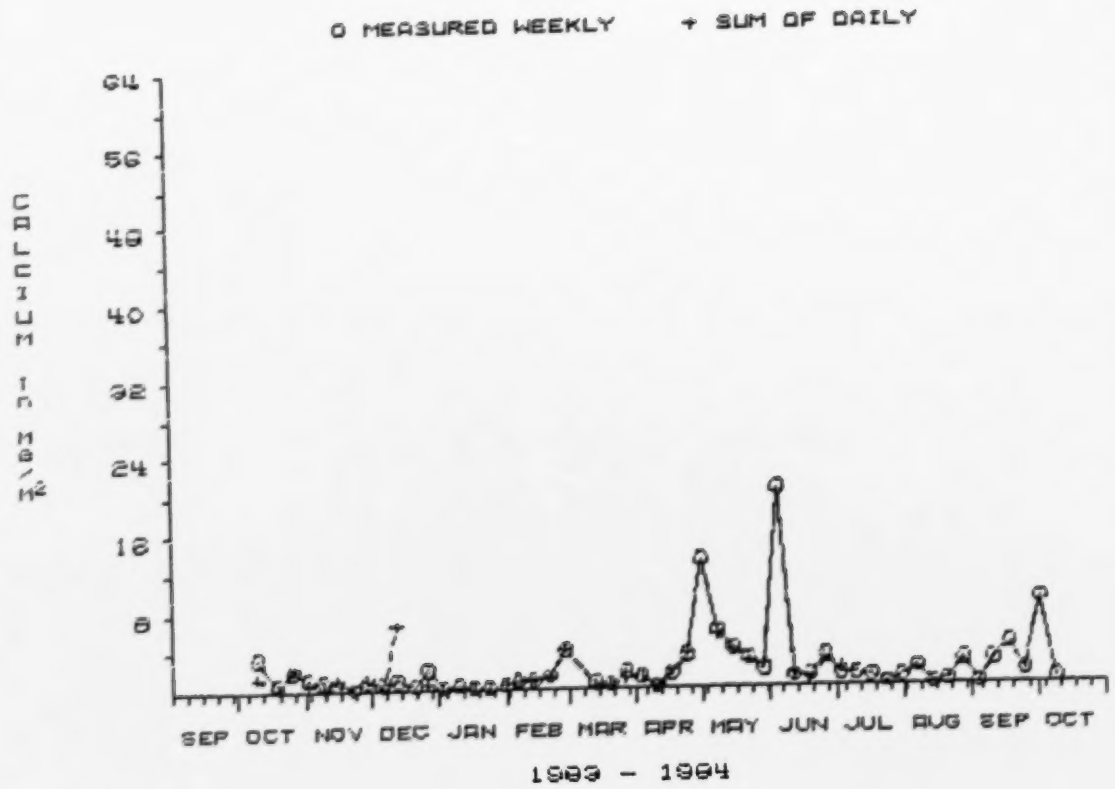

FIGURE C-15. Comparison of measured weekly and composited daily calcium deposition for Underhill, Vermont.